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Detritus - Multidisciplinary Journal for Waste Resources and Residues - is aimed at extending the "waste" concept by opening up the field to other waste-related disciplines (e.g. earth science, applied microbiology, environmental science, architecture, art, law, etc.) welcoming strategic, review and opinion papers. **Detritus is indexed in Emerging Sources Citation Index (ESCI) Web of Science, Scopus, Elsevier and Google Scholar**. Detritus is an official journal of IWWG (International Waste Working Group), a non-profit organisation established in 2002 to serve as a forum for the scientific and professional community and to respond to a need for the international promotion and dissemination of new developments in the waste management industry.

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Editorial

WHAT IS THE FUTURE FOR PUBLIC COMMUNICATIONS ABOUT WASTE AND RESOURCES?

Contemporary society faces many pressing problems, of which the development of a sustainable approach to waste and resource management is just one. Enabling effective resource management requires active public engagement and motivation – alongside appropriate infrastructure and service provision - and this is hugely challenging. Many political, environmental, social, technological, legal and economic approaches have been trialled, but only slow progress has been achieved thus far in many settings.

Communication is a vital tool for scientists' findings to make some form of impact. Research around topics such as climate change, water pollution and food waste often needs to inspire changes in public knowledge and behaviour to catalyse necessary, rapid public action.

When it comes to more emotive topics such as climate change and recycling/incineration, the public may have strong responses to media communications that highlight the potential severity of future events and situations. However, information on the actions or changes they should make to tackle the issue can be lacking (Balmford et al., 2004). Raising awareness may motivate people in a general sense but actual information on necessary and beneficial actions are a vital part of science communication for resolving environmental issues.

There are many traditional methods of public communication about waste. Advisory panels, committees and fora, consultation papers and requests for comments have narrow reach and tend to focus on "experts" not the public. Methods such as community information (posters, leaflets, doorstepping, focus groups), public meetings (private or public), citizens' juries & parliaments, workshops & seminars, stalls at fairs / events, and mass media campaigns (radio / TV / the Internet) tend to have limited, mainly short-term impacts (Timlett and Williams, 2008). Even very high-profile campaigns – including the use of popular children's TV shows (Sesame Street, Captain America, The Wombles, The Regenerators) to highlight the problem of littering - and the Waste and Resources Action Programme's highly acclaimed "Love Food Hate Waste" campaign (Yamakawa et al., 2017) - did not stop litter and food waste, respectively, from continuing to rise. These methods have tended to assume that scientific and public views on such topics are divergent, assuming that the public's knowledge is incomplete and/or flawed. Communication efforts focused on public education and awareness raising ensue, failing to guide and inform the public towards environmentally beneficial actions and behaviours (Brock et al., 2022).

In terms of stimulating public actions, Timlett and Williams (2008) reviewed some of the most popular communication and behaviour change methods used in the waste and resources sector to encourage positive recycling behaviour. This review showed that simple feedback can be highly effective when it is regular, incremental, well communicated, monitored and reinforced. Expensive, complicated options are not always required and positive behaviour change can be achieved using relatively cheap, "low-tech" methods.

In fact, recent research (Cooper and Nisbet, 2016) has highlighted that ideology, not knowledge, best predicts environment-related attitudes and behaviour, leading researchers to move away from investigating cognitive bias towards investigating the effectiveness of e.g. emotion-based approaches (Brock et al., 2022).

Our "communication problem" is particularly obvious in waste management due to the scale and immediacy of the issues to hand and the impacts of failing to make progress towards sustainable use of natural resources in the face of rising human population and increasing demand for goods and services. Whilst the public may be aware of general waste management related issues, they may be unaware of new and emerging issues and the collective positive impacts they can cause by changing their behaviour. This is significant, since: i) citizen support is essential for implementation of new and/or ambitious waste-related policies, and ii) populism and its rhetoric are currently burgeoning, often influencing the public away from policies based on science-based evidence, Hence, in order to communicate waste-and resource-related information in a way that is more accessible to the public, and actually leads to desired behaviour change, new methods must be explored. Citizen support is essential for implementation of ambitious waste-related policies, strategies, and action plans.

Hence a vital research question that needs to be answered is "What is the future for public communications about waste and resources?" This gives rise to other, more specific questions: Are traditional methods of communication waning? Are some of these methods still relevant in the social media age? If so, which methods, and why? Might emotion- and/or ideology-based approaches be more effective? What is the role of inter-generational influence and role models in providing effective and trusted communica-

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tion? Who is trusted to give environmental messages and why are they trusted? Might personal feedback methods work and be more cost-effective in the longer term? This is by no means and exhaustive list of concerns and questions!

As we move rapidly towards the need for urgent behaviour change to ensure climate change and resource-related targets are met by 2030, these questions must be answered. We need to identify which methods are best used to communicate and consult with the public about environment, waste, and resources, and why, providing evidence to support decision-making. And we must be disciplined - anecdotes are interesting but robust, meaningful and representative evidence must be at the heart of the decisions we make and the directions we travel.

Scientists and engineers need to answer this big question now. There is no more time for procrastination when it comes to addressing the global environmental issues of our era.

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CONSIDERATIONS ON WASTE CHARACTERIZATION AND THE PRODUCTION OF ENERGY: HOW USEFUL CAN WASTE BE?

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ABSTRACT

The proposed work reports a compilation of municipal solid waste composition in several geographies, discussing the impacts and repercussions of different waste classification nomenclature and related definitions. In addition, different scenarios are evaluated using the average waste composition in each location to further describe the possibility of covering the energy demand in those places, with energy produced from waste. For that, the thermal conversion efficiency of each Waste-to-Energy (WtE) procedure (combustion, incineration, hydrothermal liquefaction, pyrolysis, gasification, and plasma gasification) was used, so that a comparison of performances is put forward, to potentially aid in policy- and/or decision-making processes. Hydrothermal liquefaction presented higher efficiencies, followed by gasification-based techniques. Incineration, combustion and pyrolysis show a declining performance. In terms of waste production, OECD countries exceeded the average waste production values as well as the energy demand per capita, while Europe and Central Asia depicted the lowest contribution of energy produced from the waste generated.

1. INTRODUCTION

New policy packages and government plans and targets such as the RePowerEU plan and the Fit for 55 package (European Union), the Inflation Reduction Act (United States), the Climate Change Bill (Australia), and the GX Green Transformation (Japan), are setting the tone to an accelerated clean energy development this decade, especially in advanced economies. A decreasing demand for all fossil fuels by 2030 is expected and already on the march in advanced economies, however these measures take time to roll out (Agency, 2022; Bois von Kursk et al., 2022). To reduce the dependency on fossil fuel imports, especially in Europe, short-term actions are required, giving consumers a key role in terms of behaviour change; nevertheless technological advances namely in energy production systems are also a major driver for this transition. While in emerging markets and developing economies the demand for fossil fuel upsurges more slowly, the slowdown in fossil fuel demand progress is led by China, where the combination of decelerating the economic growth and the policy efforts lead to a peak in emissions (Agency, 2022).

The importance of waste management is emphasized in the 2030 agenda for Sustainable Development Goals (SDG) (Nations, 2016). Waste may be seen as a multidimensional subject with technical, environmental, economic, social, and ethical dimensions, highlighting major disadvantages and differences of marginalized communities over less difficult contexts (Nations, 2021). Nevertheless, by means of the concept of Waste-to-Energy (WtE), waste is regarded as a raw material for alternative energy production, ideally replacing the use of fossil-based options (Ramos & Rouboa, 2020). This enforces the perspective of waste as a valuable resource, namely contributing to the clean energy transition, diminishing the negative impacts usually related to it. Indeed, the values of sustainable production and consumption, as well as circular economy principles are also being met by this approach, as a strategy to close the loop on residues and comply with the SDGs (E. Commission, 2020).

Figure 1 shows the progress of two key energy system indicators for the global energy transition envisioned by the International Renewable Energy Agency (Gielen et al., 2019) (on the left), as well as the average global share of waste treatment as reported by the World Bank Group (Kaza, Yao, Bhada-Tata, & Woerden, 2018) (on the right).

From Figure 1 it is observed that although the energy consumption per capita is expected to decrease roughly 25% until 2050, the required levels will still be high while more environment-friendly production procedures are deemed to be used (lowering CO_2 emissions). Meanwhile, in what regards waste treatment techniques, these are somehow misadjusted, open dumps and landfill combining a great

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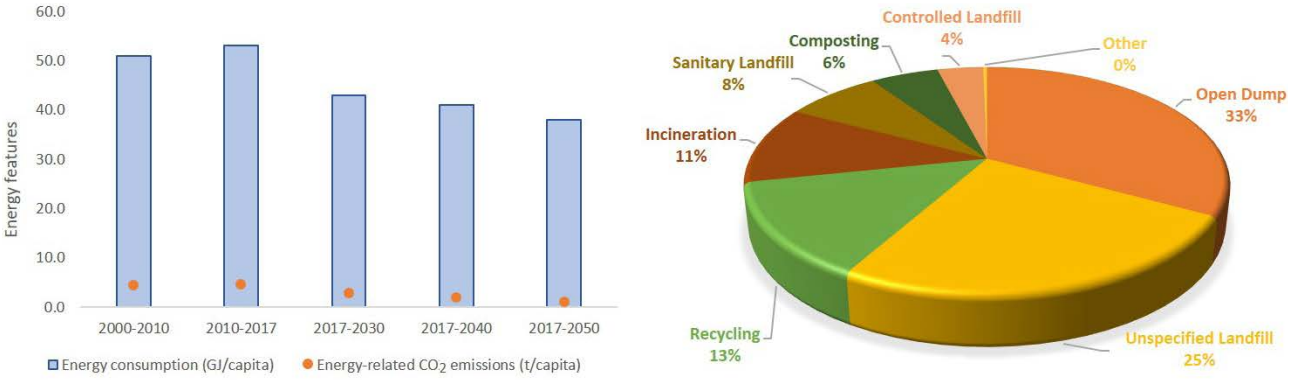

FIGURE 1: Energy consumption and emissions data (on the left); global shares of treatment and disposal of waste (on the right).

share of disposal options, while the thermal procedures depict a low portion of the share. This means that there is space for the thermal treatments' segment to grow, once their efficiency and environmental character is proved (Sun et al., 2020). This will add value to most residues at their end-of-life stage, widening the spectrum of available WtE techniques, which enhances the sustainable energy production to potentially meet the population's energy demand.

This work proposes a screening through waste composition across distinct world regions, discussing aspects related to waste production and classification. Also, the possibility of producing energy through several WtE to fulfill part of the energy demand in those places is put forward, as a novel feature in this type of literature reviews, especially because this is done for distinct waste-to-energy techniques, enhancing the body of knowledge in the field.

2. MATERIALS AND METHODS

2.1 Bibliographic review

Recent literature in the topic was searched with significant keywords in relevant scientific databases (Web of Science, Scopus, Science Direct, Google Scholar). The keywords applied were "municipal solid waste composition", "MSW composition", "municipal solid waste characterization", "MSW characterization", "urban waste composition", "urban waste characterization", "urban residues composition", and "urbanc residues characterization" (MSW stands for Municipal Solid Waste).

The entries retrieved were reviewed for duplicates, and individually inspected for effective content, a shortlist of pertinent works being compiled in Table 1 (*please see the supplementary material*).

2.2 WtE conversion efficiency

The energy efficiency used to perform the conversion calculations in this work was previously achieved in other works (shown in Table 2), namely conducted for the evaluation of the environmental assessment of the WtE techniques such as incineration, gasification and plasma gasification (Lombardi, Carnevale, & Corti, 2012; Ramos & Rouboa, 2020; Ramos, Teixeira, & Rouboa, 2019), or retrieved from dedicated literature for pyrolysis (D'Alessandro, D'Amico, Desideri, & Fantozzi, 2013), combustion (D'Alessandro et al., 2013; Viganò, Consonni, Grosso, & Rigamonti, 2010) and hydrothermal liquefaction (University, 2013; B. Zhang et al., 2017). Gasification involves the partial combustion of biomass to generate flammable gases like CH_4, H_2, and CO, which are often mixed with other substances like benzene, toluene, aliphatic hydrocarbons, and tars, resulting in a mixture known as syngas. This gas fuel is created by subjecting biomass to high temperatures exceeding 800°C within an environment of oxygen, air, or steam (Ramos, Monteiro, & Rouboa, 2019). Plasma consists of ionized gases at elevated temperatures, enabling rapid and effective heat transfer through electrical discharge. This method significantly enhances the conversion process due to the exceptionally elevated temperatures, causing even the most resistant inorganic compounds that typically resist gasification to "melt" and undergo transformation (Boulos, Fauchais, & Pfender, 2013). In the process of pyrolysis, thermal energy is utilized to break down the chemical bonds within materials (Elgarahy et al., 2021). This technique finds applications across a range of domains, including the chemical industry, as well as in the study of natural and biological substances, forensic resources, and trace-level analysis (Wampler, 2006). Combustion employs air as the oxidizing agent to generate heat energy. In this method, the feedstock is subject to oxidation, resulting in the creation of high-temperature gases ranging from 800°C to 1000°C. These gases are then utilized to generate steam or heat (Elgarahy et al., 2021). Hydrothermal techniques break down the solid biopolymeric components of the feedstock, yielding valuable high-energy products and chemicals. These processes occur within a temperature range of 250°C to 375°C and under pressures ranging from 4 MPa to 22 MPa. As the temperature rises, the viscosity of water decreases, enhancing the efficiency of mass transfer and diffusion coefficients (M. Kumar, Oyedun, & Kumar, 2018).

As main assumptions, zero losses in waste conversion and a constant average waste composition were adopted, in order to extrapolate the electricity produced from the MSW generated in several parts of the world. This is a feasible approach as seen in literature (Hoornweg & Bhada-Tata, 2012).

2.3 Contribution to the electricity consumed

An estimation of the share of energy hypothetically

produced from the waste generated per capita was conducted, considering the average yield and composition of waste, as well as the average electric consumption in each area (Bank, 2018; Hoornweg & Bhada-Tata, 2012). The proportion of the electrical demand per capita served by the energy achieved from the thermal conversion of the MSW generated by each person (which is then used as electricity) was calculated through Equation 1, assuming no losses in conversion efficiency.

$$\%\ MSW\ contribution\ = \frac{average\ waste\ yield \times WtE\ conversion\ efficiency}{\text{average electric power consumption}} \quad (1)$$

This calculation enables the proposal of a parameter relating the electricity consumed and the waste generated in each part of the world, as a potential measure of economic development. This is mainly related to the fact that most of the nowadays' commodities depend on electric power, implying the social welfare of the population. In a previous report, this indicator has been suggested as a basis for the strategic development regarding waste management options or electrical grid planning (Ramos & Rouboa, 2020).

3. RESULTS AND DISCUSSION

3.1 Literature review on waste characterization

Table 1 (*please see the supplementary material*) presents the key composition features for the MSW described in selected literature.

3.1.1 Prevalence of MSW composition

From Table 1 (*please see the supplementary material*) it is possible to observe a prevalence of the organic fraction in the vast majority of the assessed MSW samples, depicting around 75.6% of the total share of literature assessed. It is also possible to notice that this is a dominant trend within the same country, except in occasional cases as for instance Tekirdag in Turkey (Bolukbas & Akinci, 2018), Kanpur and Hyderabad in India (Dixit et al., 2022; Singh & Uchimura, 2022), and Xi'an in China (Xiao et al., 2009), where Others has a higher fraction when compared to the remaining cities in the same countries. This is also the case for Mexico (Tsydenova et al., 2018) and Norway (Sorum et al., 2001). Actually, the Others fraction represents 11.2% of the total distribution within the assessed literature, in ex aequo with Paper. A fact possibly concurring to higher shares of the Others components is the source of energy used in those places, as for instance coal-based activities generate ashes which account for this category, whilst activities fuelled by natural gas or electricity are cleaner regarding this aspect (Grammelis, 2010; Hoornweg & Bhada-Tata, 2012).

Paper is the dominant fraction in countries such as Taiwan (Chen, 2018), Japan (Du et al., 2021), and Israel (Q. L. Zhang et al., 2012). Nottingham is an outlier to the dominance of the organic fraction seen in other UK locations, Paper being the prevailing component in this city (D. Wang et al., 2018). Other representations of this phenomn are Mavallipura (India), where Plastic is the higher fraction seen in the reported MSW sample (Naveen, 2018), and Ilorin (Nigeria), where the plastic fraction prevails over the paper fraction seen in Lagos (Ibikunle et al., 2020).

Metal, glass, textiles and wood are not considered the main components in any of the literature reported. Oppositely, these are most of the times the less significant fractions as seen for the case of Taiwan (Chen, 2018), Thailand (Outapa & Roi-et, 2018), Indonesia (Indrawati & Purwaningrum, 2018), Saudi Arabia (Osra et al., 2021), Romania (Ciuta et al., 2015), China (Ding et al., 2021; Du et al., 2021; Xiao et al., 2009), and Singapore (Bolukbas & Akinci, 2018; Du et al., 2021).

This might sometimes be explained by the different sampling and characterization methods, which may attribute different categories for the same type of residues (for instance classifying some residues as Others instead of a defined category), or even by the fact that there is no detailed information available in literature (Hoornweg & Bhada-Tata, 2012; Parfitt & Bridgwater, 2008; Ramachandra et al., 2018; Singh & Uchimura, 2022). The rapid urbanization of some developing countries may also contribute to the outliers in the waste composition and management systems, as seen in Santa Cruz (Bolivia), parameters such as household size, education level, and number of children in the family being considered (Lozano Lazo et al., 2023). Section 3.1.2 discusses the contribute of waste terminology and categorization in more detail.

Overall, high-income regions produce relatively less organic waste than middle- and low-income areas, dry waste (in general recyclable - plastic, paper, cardboard, metal, and glass), accounting for higher shares of waste. Middle-income countries generate more levelled proportions of organic and recyclable waste increasing as economic development levels decrease, while low-income countries report only around 20% of recyclable materials. Averagely speaking, all regions seem to generate around or more than 50% of organic waste, exceptions being made for Europe and Central Asia and North America, where higher shares of dry waste are reported. This is in line with The World Bank projections (Kaza et al., 2018).

3.1.2 Discrepancies in definitions and standards

The differences in terminology, concept meaning and law enforcement in what relates to waste management may lead to situations where the same component may be understood as recyclable in one country, energetically valorizable in another region and general waste in a different location (Kawai & Tasaki, 2016; Park & Lah, 2018). For instance, under the EU legislation, less than 27% of the MSW produced in 2015 was recycled, whereas under a more conservative system as the one in South Korea, a recycling rate of 59% was reported for the same year, and roughly 30% in the USA (Development, 2016). Nonetheless, if the EU standards were applied for the South Korean and American systems, recycling rates as high as 70% and 40% would be respectively achieved (Park & Lah, 2018). Another example of incongruence is the fact that 17% of plastic waste worldwide is collected for recycling, although there are large differences between regions: for example, in Europe 25% is collected for recycling while less than 10% is collected in the United States. Also, recycling rates are completely different depending on the waste fraction considered and the interest it brings: plastics are much less likely to be recycled than steel, aluminium and paper (Agen-

cy, 2022). Indeed, the effect of variables such as incentives to source reduction, collection and recycling rates, and the existance of composting and incinerating facilities are totally distinct depending on the income level of the world region (Hoornweg & Bhada-Tata, 2012). All these factors account for inconsistencies and hamper an archetype pathway towards revalorizing waste streams and avoiding landfilling and open dumping.

Apart from the perceived different standards and waste management legislation pieces in distinct world locations/ socioeconomic organizations, waste availability also promotes dissimilar composition for the same kind of waste streams, if a specific composition has to be met depending on the purpose (Bergeron, 2017). Waste composition and production rate may be considered two of the central contributions for the enhancement of waste management systems, helping to shape policies to meet the stated regulations (Engineering, 2011). It should also be noticed that waste yields might be incorrectly estimated when inadequate population data is considered (Hujare & Telsang, 2020). Besides, by overlooking the closed characteristics of compositional waste fraction data, the statistical analyses can lead to illegitimate or misleading results (Edjabou et al., 2017). Bottom-up and topdown methods for analyzing the physical composition of MSW have been discussed by Zhou et al (Zhou et al., 2022) in Wuhan, China.

Depending on the characteristics of the area where the waste is generated, it may show completely distinct profiles, which will furthermore define its potential revalorization (Adeniran, Adelopo, Aina, Nubi, & Apena, 2019; Baran, 2018; Ciuta et al., 2015). Events related to tourism, geophysical constrains or socioeconomic and cultural activities also promote discrepancies in waste composition in defined locations (Bolukbas & Akinci, 2018; Diaz-Farina, Díaz-Hernández, & Padrón-Fumero, 2020; Ibikunle et al., 2020; Park & Lah, 2018). This may sometimes trigger mismanagement practices if the system reveals itself insufficient to deal with amounts of waste larger than usual, unbalancing the conventional or expected residues' streams, due to operational and governance weaknesses (Abdulredha et al., 2020; Diaz-Farina et al., 2020). Climate conditions may further endorse changes in waste composition interfering with parameters as moisture content, type and amount of biodegradable and recyclable components (Hoornweg & Bhada-Tata, 2012). The existence of dedicated and suitable containers according to the separation legislations in place is also a major conditioning factor in what regards waste collection, categorization and management (Hogg & Consulting, 2016; Hoornweg & Bhada-Tata, 2012).

3.2 Electrical needs vs waste produced

3.2.1 World regions classification

According to the World Bank, countries may be classified upon their income level, the world's economies being allocated to one of four income groups — low, lower-middle, upper-middle, and high income (Rompaey, Metreau, & Eapen, 2022). In terms of geographical areas, the classification is based on the regions used for administrative purposes by the World Bank (Group, 2017). Figure 2 depicts the geographical classification, and Figure 3 presents the relation between the income level and the regional classification.

This classification was utilized in this work as a guidance to better discuss the results presented in the following sections. For the sake of simplicity, acronyms for the world regions were used, as follows: MENA – Middle East and North Africa; AFR – Sub-saharan Africa region; EAP – East Asia and Pacific; ECA – Europe and Central Asia; OECD – Organization for Economic Co-operation and Development; SAR – South Asia region; LCR – Latin America & the Caribbean region.

High-income countries generate circa 34% (683 million tonnes) of the world's waste, although they represent only 16% of the world's population (Kaza et al., 2018). Overall,

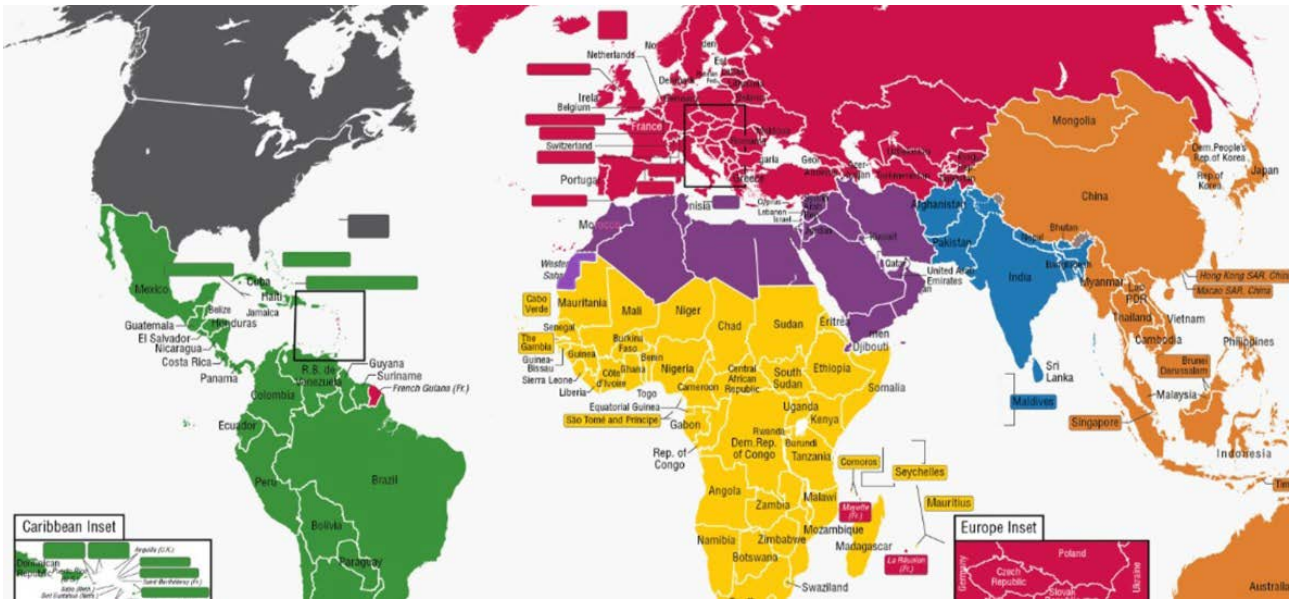

FIGURE 2: World Bank grouping of countries by regions, including economies of all income levels (adapted from Group, 2017).

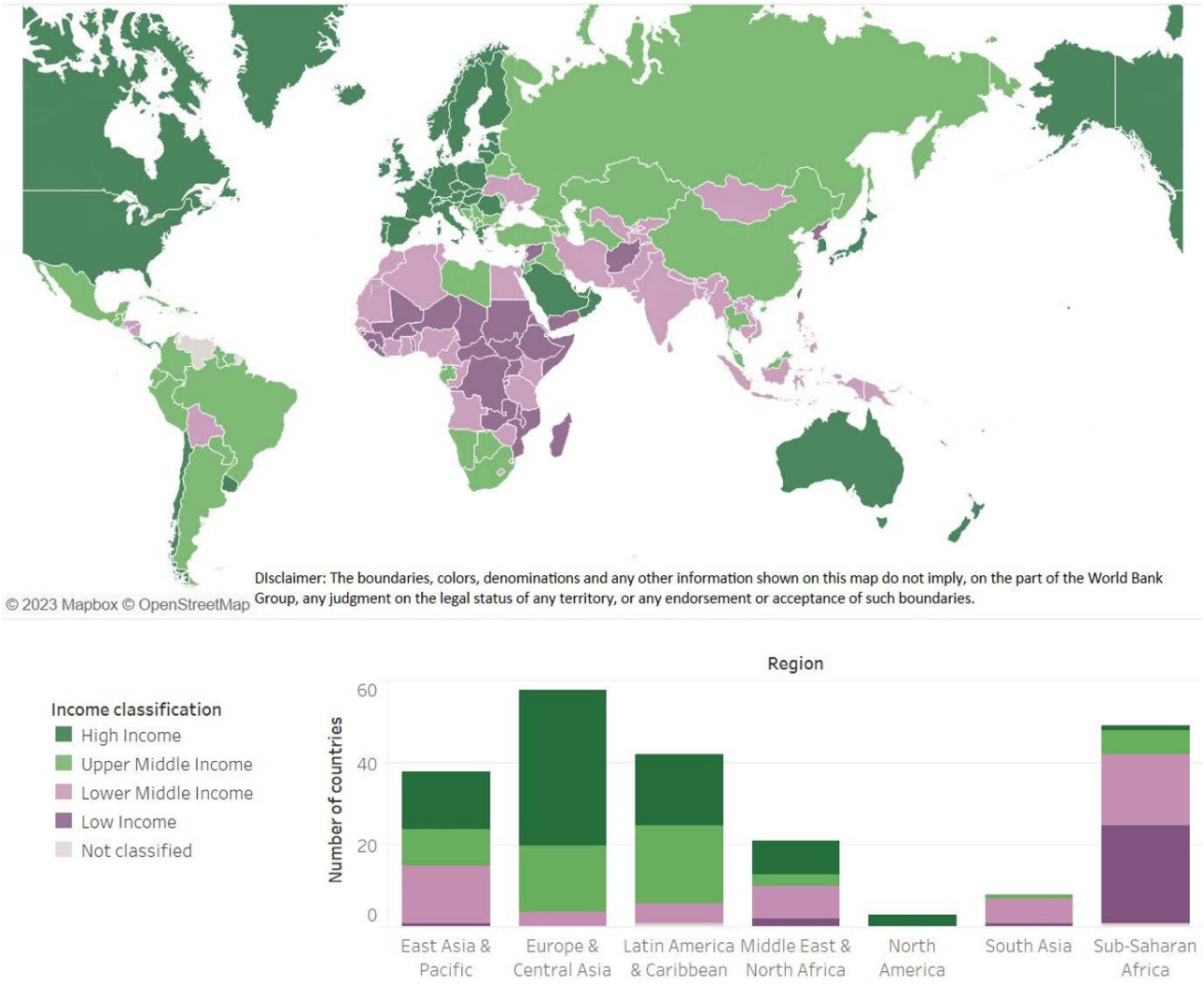

FIGURE 3: World Bank country classification by: top) income level; bottom) share of income levels by world region (adapted from Rompaey et al., 2022).

low-income countries collect around 48% of waste in urban areas, this proportion significantly dropping to 26% in rural areas. SAR collects about 44% of waste, whereas ECA and North America collect more than 90% of waste (Kaza et al., 2018). Generally speaking, the higher the income level and rate of urbanization, the greater the amount of solid waste produced (Hoornweg & Bhada-Tata, 2012).

3.2.2 Relation between energy consumption and waste production

Computing the waste production against the electricity demand for all the world regions, a major trend can be seen, as shown in Figure 4. Developed countries reveal higher shares of electricity demand and waste production, whilst developing regions present inferior values.

Based on the results presented in Figure 4, OECD is the part of the world where more waste is produced (almost half of the world waste according to (Hoornweg & Bhada-Tata, 2012)), followed by regions such as ECA, LCR, and MENA. EAP and AFR show lower waste production yields, while SAR is the region where less waste is produced per capita. In terms of income, high income countries are responsible for 46% of the total waste generated worldwide, while upper-middle income countries generate 19% of this share, lower-middle income regions contribute with 29%, and low income countries are responsible for a 6% share (Hoornweg & Bhada-Tata, 2012). Likewise, the collection rates show a similar profile by geographical area, higher collection rates being seen in higher income regions.

On the same trend, OECD is the major power consumer, followed by ECA and EAP; MENA and LCR show lower energetic needs, whereas SAR and AFR exhibit energetic demands one order of magnitude lower the rest of the world. This is in accordance to the fact that over 620 million people living in Africa do not have access to electricity (Bois von Kursk et al., 2022). Nevertheless, as stated by Kaza et al (Kaza et al., 2018), the fastest growing regions in terms of waste production are AFR, SAR and MENA where, by 2050, total waste generation is expected to be three-, two-, and two-fold respectively. The energetic demand has been raising and will continue to grow, mainly due to the ever-increasing will of developing countries to thrive and meet

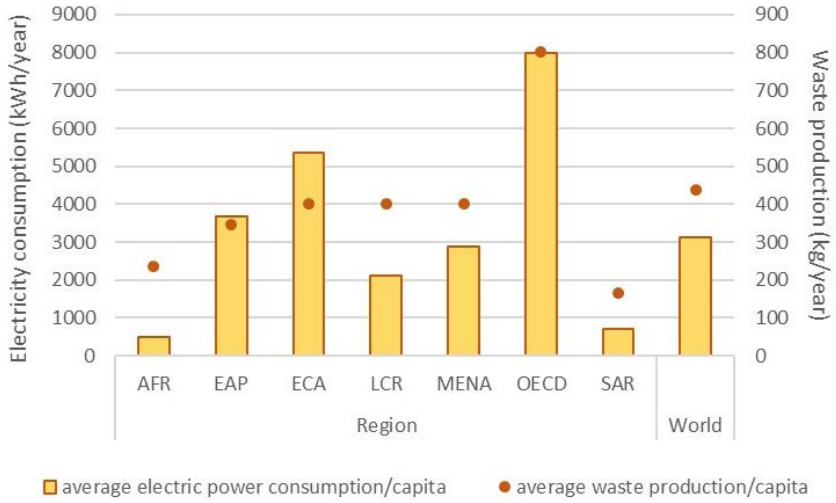

FIGURE 4: World data for electricity consumption vs waste generation.

their socio-economic needs (Bois von Kursk et al., 2022). In these regions, more than 50% of waste is currently sent to open dumps, with the associated environmental, health and socioeconomic implications (Hoornweg & Bhada-Tata, 2012). Therefore, this requires urgent action, one of the suitable options being to convert this concern into an opportunity in the energy sector (Agency, 2022; Chand Malav et al., 2020; U. N. B. Commission, 1987; Grammelis, 2010).

This energy transformation fosters socio-economic benefits as enhanced economic growth, new jobs and overall prosperity, while reduces net costs and environmental impacts (Gielen et al., 2019; Ramos & Rouboa, 2020).

3.2.3 MSW contribution to the energy demand

Depending on the waste composition, its production rate, and the power needs of the population per area, different contributions from the conversion of the residues into energy are expected. Table 2 presents the hypothetical share of electricity produced by the thermal conversion of MSW in several regions, for each WtE.

It should be noted that the values seen in Table 2 must be faced cautiously and within the defined boundaries for each scenario. Indeed, it shows that, according to the location and socioeconomic context, the thermal treatment of the waste produced per capita may provide between 2% and 53% of the electricity consumed by each person. WtE techniques such as hydrothermal liquefaction show potential to cover a higher share of the energy needs (up to 53% input), especially in AFR and SAR, followed by the gasification-based technologies (6%-41% contribution). Incineration depicts a lower performance, granting 4% to 23% of electricity coverage, followed by combustion (2% to 15% share) and pyrolysis with 2% to 12% contribution. This is supported by literature referring to the production of energy from biosolids and other residues (Elgarahy et al., 2021; Grammelis, 2010; Jung et al., 2021; Rezaei, Ghobadian, Samadi, & Karimi, 2018; Vallejoa, Díaz-Roblesa, Cubillosa, & Perez, 2020). Elgahary et al (Elgarahy et al., 2021) refer the economic aspects of the thermochemical conversion as a promosing integrated approach, while Jung et al (Jung et al., 2021) discuss the suitability of livestock manures to be used as different biofuels instead of using edible crops as biomass feedstock for the same purpose. Rezaei et al (Rezaei et al., 2018) review the sensitivity analysis of different scenarios for choosing an effective and efficient technology for the conversion, comparing incineration and gasification; whereas Vallejoa et al (Vallejoa et al., 2020) compare gasification to hydrothermal carbonization. Complementarily, current practices, challenges, and future opportunities of using MSW as a renewable source of energy were reviewed in topical works (Agency, 2013; Chand Malav et al., 2020; Foster et al., 2021; Nunes, Matias, & Catalão, 2017; Ofori-Boateng, Lee, & Mensah, 2013). Chand Malav et al (Chand Malav et al., 2020) put forward a number of recommendations for improving the currently implemented solid waste management in the Indian context, Foster et al (Foster et al., 2021) examining the processes and barriers related to the conversion of solid residues in the UK; moreover, Nunes et al (Nunes et al., 2017) review the main parameters that influence the quality of biomass for application in WtE in Portugal, while Ofori-Boateng et al

TABLE 2: Average values for waste production and electric power consumption per capita, and the potential contribution of thermally converted MSW worldwide.

Location	MSW contribution to the energy consumed (%)					
	C	HTL	P	I	G	PG
AFR	14.62	52.63	11.70	23.28	40.93	41.23
EAP	2.81	10.10	2.25	4.47	7.86	7.92
ECA	2.22	8.01	1.78	3.54	6.23	6.27
LCR	5.61	20.21	4.49	8.94	15.72	15.83
MENA	4.16	14.96	3.33	6.62	11.64	11.72
OECD	2.99	10.77	2.39	4.77	8.38	8.44
SAR	6.91	24.89	5.53	11.01	19.36	19.50
World	4.17	15.01	3.34	6.64	11.67	11.76

C: Combustion; HTL: Hydrothermal Liquefaction; P: Pyrolysis; I: Incineration; G: Gasification; PG: Plasma Gasification

(Ofori-Boateng et al., 2013) refer the perspective of waste management on Ghana.

Taking into consideration the geographies evaluated in this work, OECD countries depict one of the lowest coverages of electrical demand provided by the produced MSW fraction (2% to 11%), despite being the ones with higher MSW yields. This is also seen for ECA, where the coverage is even lower (2% to 8%), and for EAP (2% to 10%). The MENA region follows, MSW contributing with 4% to 15% to the electrical demand, while LCR shows contributions ranging between 5% and 20%.

From this, socioeconomic correlations related to the population habits and access to energy may be implied, higher income countries producing more waste and requiring more energy than lower income countries, where the energetic needs are met more effortlessly, while waste is produced in a significantly lower amount. This is in accordance with expected trends seen for other indicators (Ramachandra et al., 2018; Ulgiati et al., 2011).

4. CONCLUSIONS

After a review of the most recent literature concerning MSW composition, major trends could be seen especially in what relates to the income level and geographic positioning of the regions assessed. Then, an estimation of the electricity share potentially produced from the waste generated per capita in the world was put forward. Comparing the performance of six different Waste-to-Energy techniques in what regards producing energy for the assessed regions, hydrothermal liquefaction depicted higher efficiencies, followed by gasification-based techniques. Incineration, combustion and pyrolysis displayed a decreasing performance.

Major contributions were observed for Sub-Saharan Africa and South Asia due to the lower electrical demand in these areas, though OECD countries clearly surpassed the average waste production values as well as the energy demand per capita. Latin America & the Caribbean and Middle East and North Africa regions followed; East Asia and Pacific, and Europe and Central Asia depicting the lowest contribution of energy produced from the waste generated.

The main general take-away message from this work is that waste cannot be "thrown away". Whatever the disposal option is, it remains in our planet affecting our lives in one or another way. It depends on us to take advantage of the situation already in place and take it as an opportunity to evolve in a more environment-friendly direction. Hence, behavioural changes from the end-users would contribute both to diminish the amount of waste created as well as the energetic needs associated to a comfortable and wealthy way of living; while on a macroeconomic level, overall rethinking the current production and supply chains would also foster a more sustainable life on Earth.

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APPLICATION OF A GAS-SOLID FLUIDISED BED SEPARATOR FOR ALUMINIUM-COPPER SCRAP RECYCLING

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ABSTRACT

The EU's circular economy concept necessitates the recycling of material streams used once or multiple times into the production–consumption cycle again and again. The commonly known problem – that the number of recycling cycles of plastics is limited – drives the economy towards metal usage again, because metal recycling cycles are limitless. Therefore, the efficient and economic separation of mixed aluminium and copper scraps in the 30–100 mm particle size range is an important issue for our society. In this study fundamental and applied research was carried out for the application of a gas-solid fluidised bed separator for aluminium-copper scrap recycling. A laboratory scale aero-suspension dense media separator was developed. Fundamental fluidisation experiments were carried out with this device and a powder rheometer. Afterwards pilot-scale and later industrial-scale separators were designed and built. The results indicate that the well-known Ergun fluidisation model can be the basis of a new process engineering design method for sizing dry fluidised bed separators.

1. INTRODUCTION

Among humanity's greatest challenges today is the provision of material and energy for civilised life. Even though the collection and recycling of scrap metals is only a very small part of the whole, if we do it in an energy-efficient way (Hou et al., 2022; Zhumadillayeva et al., 2020), we contribute to the goal of securing material for mankind. This is the research gap this paper addresses. The fluidised bed aero-suspension dense media separator is a well-known type of equipment (e.g., Anjaneyulu & Khakbar, 1995; Basu, 2006; Beeckmans & Minh, 1977; Gibilaro, 2001; Sahu et al., 2009; Fan and Zhou, 2021), however its design is still based on experiment, process engineering design methods need to be further improved.

Based on its operating principle, there is a solid-gas fluidised bed made by blown-in air from the bottom into the bulk granular separation medium. The mixture density of the fluidised solid-gas dense media can be controlled by the quantity of the air blown in. The heavier particles of the feed will sink, and lighter particles will float. Compared to wet dense media separation, there is no need for any liquid, and therefore no need for the clarification for the separated products or a water handling system. The dry fluidised bed method of separation needs to be explored because it produces low pressure drop and high efficiency (Anam & Ikhwan, 2020) and that helps with fulfilling the targeted aim of waste-to-material recycling for the circular economy. Therefore, dry dense media separators are widely applied in the industry. The first application of fluidisation was invented by Brötz in 1900 (Ghosh, 2013). Brötz applied a counter-current water flow to loosen a sand water filtration bed. Dry dense media separation is widely applied in the pharmaceutical industry (Dévay, 2013) and in waste management (Everett & Peirce, 1990). A gas-solid fluidised bed separator was applied on a laboratory scale for shredded municipal bulky solid waste separation (Sekito et al., 2006). The work of Sekito et al. (2006) was later further improved by Yoshida et al. (2010), when the chlorine content of processed plastic part of municipal solid wastes was significantly decreased by a fluidised bed dry separator. Separation of harmful impurities from refuse derived fuels (RDF) was carried out in a solid-gas fluidised bed (Krüger et al., 2014). There are other applications of dry fluidised bed separation technology for waste processing; Oshitani et al. (2003) used this technology for recycling automotive shredder residue materials.

There are several scientific and practical challenges to be solved for the development of a separation machine. The most important might be how to establish homogeneous solid-gas distribution in the fluidised bed. There are several unwanted phenomena that might occur during insufficient bed operation, such as bubbling, slugging, channelling and

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agitation, and turbulent fluidisation (Ghosh, 2013). Figure 1 shows the typical pressure loss of fluidised solid-gas beds as a function of the air velocity (Dévay, 2013; Thanh & Duc, 2020).

When the flow rate of air blowing is increased from 0 up point A the solids are still packed in the bed and the pressure loss increases linearly with air velocity because of the laminar flow between the particles (Dévay, 2013). Between points A and B, the velocity increases exponentially and from point B the solid particles start to levitate. Between points B and C they may have better orientation and that decreases the resistance; therefore, the pressure loss also decreases a little. From points B to E good fluidisation can be established. In this desirable zone the particles typically do not contact, they are levitating in the air stream, and the pressure loss does not depend on the fluid velocity, nor does it depend much on the solids concentration either in this zone. From point E, the transport of the particles starts, which is another process, namely pneumatic transport. This is clearly avoidable in fluidised bed technologies. Figure 1 is extremely important for the process engineering point of view. The air flow rate range between points D and E is small; it is a practical challenge to establish stable conditions here. The density of the fluidised solid-gas bed depends on the air flow rate in zone D-E and this range is limited. The density of the fluidised solid-gas bed is crucial for the separation because this is the cut density. The density of the applied solids as separation medium basically determines the mixture density. However, theoretically it is possible to set a different fluidised solid-gas bed density and therefore a different cut density by changing the air flow rate. According to Zhou et al. (2019) the bed density in the aero-suspension dense media separator can be determined theoretically for a given fluidisation air velocity using the two-phase theory, but empirical validation is necessary. Li et al. (2017) applied CFD techniques for fluidised-bed separator optimisation by using the composite force field or flow field to enhance the recovery of coarse particles and expand its application in the coarse coal slime separation and metal beneficiation. Zhao & Wei (2000) measured the rheological properties of fluidised aero suspensions with a settling body measurement device. If the solid-gas

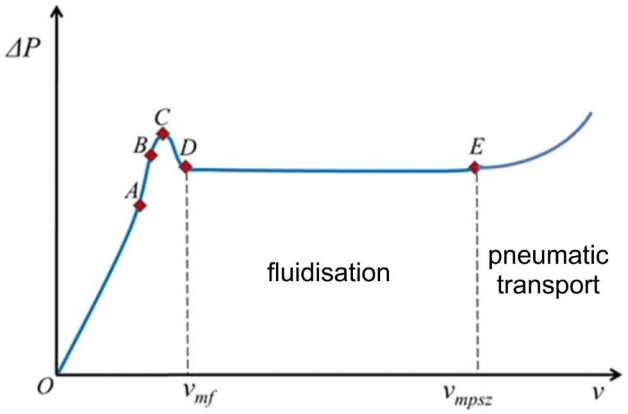

FIGURE 1: The pressure loss of fluidised solid-gas beds as function of the air velocity (Dévay, 2013).

two-phase system is fluidised the mixture behaves like a one-phase fluid, and the rheological properties of this mixture can be interpreted and measured. However, if the fine solids are not fluidised, they behave totally differently; the phenomenon of powder flow happens in this case. According to Zhao & Wei (2000), fluidised aero suspensions are typically Bingham plastic fluids with two rheological features; namely, their viscous flow can be characterised by the yield stress and the plastic viscosity.

Thanh & Duc (2020) summarised their theoretical and empirical results on dry fluidisation applied for the drying of refined salt. They comprehensively summarised the different theoretical models for the determination of the minimum fluidisation velocity in the literature. This is not repeated here (the equations of Kozeny-Carman, Wen-Yu, Beayens-Geldart, Goroshko, Goroshko-Todes, Leva and Kunii-Levenspiel are not); only the equations given afterwards are reported. The first equations and model of the field were published by Ergun in 1952. According to Ergun (1952), at the point of the "minimum particulate fluidisation state" (point D in Fig. 1) the air stream must have sufficient pressure and velocity to pass through the static bed of the dense fluidisation medium. The dense fluidisation medium can be characterised by the mean particle size (d_p), mean shape factor (F), mean particle density (r_p) and the void fraction (porosity) of the solids in the bed (e_{mf}). The applied shape factor here is the so-called surface proportional one. The volume of a non-spherical particle has to be determined first, and then the volume equivalent particle diameter can be calculated. The surface proportional shape factor is the ratio between the surface of the original particle and the surface of its volume equivalent sphere. Therefore, F=1 of a sphere because the specific surface of a sphere is the smallest. Physical properties (density r_f and absolute viscosity m_f) of air of the given temperature are known. The relationship between the air pressure (Dp) and minimum fluidisation velocity (V_{mf}) for any particle shape is given by Eq. 1.

$$\frac{\Delta p}{H_{mf}} = 150 \cdot \frac{(1-\varepsilon_{mf})^2}{\varepsilon_{mf}^3} \cdot \frac{\mu_f \cdot V_{mf}}{(\Phi \cdot d_m)^2} + 1.75 \cdot \frac{(1-\varepsilon_{mf})}{\varepsilon_{mf}^3} \cdot \frac{\rho_f V_{mf}^2}{\Phi \cdot d_m} \quad (1)$$

The pressure of the air stream at this minimum fluidisation point must be large enough to overcome the weight of the particles of the separation medium in the bed (Eq. 2).

$$\Delta p = \frac{m}{\rho_p \cdot A} \cdot (\rho_p - \rho_f) \cdot g \quad (2)$$

where A is the effective (used) cross section of the separator and m is the mass of the particles of the separation medium. Previously it was pointed out by Zhao and Wei (2000) that a flowing aero-suspension can be treated as a Bingham plastic behaviour fluid (equivalent liquid), but here at point D, the aero-suspension itself is quiescent. According to the model of Ergun (1952), we can talk about an air flow in the pores of the loosened particles of the separation medium with velocity v_{mf}, therefore a Reynolds number (Re_{mf}) can be defined using the physical properties of air and the $\Phi \cdot d_p$ term as the size parameter (Eq. 3).

$$Re_{mf} = \frac{\rho_f \cdot V_{mf} \cdot \Phi \cdot d_p}{\mu_f} \quad (3)$$

The gas-solid fluidised bed separator is an upgrading unit, because separation happens at a quality, namely at

the density (Drzymala, 2007; Pillay et al., 2022). In this form this unit represents a two- product separation process. An upgrading separation process can be characterised by the yield, content, and recovery or loss values (Drzymala, 2007). Mass yield of product A (γ_A) equals the mass flow rate of product A over the mass flow rate of the feed. The component content of component 1 in the feed is λ_1 and in product A is α_1. By this data the component recovery of component 1 into product A is $\varepsilon=\gamma_A \cdot \lambda_1/\alpha_1$. The component loss can be calculated similarly, representing the unsuccessful separation of component 1 getting into product B.

To address the above-mentioned challenges, laboratory-scale test equipment has been developed. Our research team has carried out fundamental examinations of different air inlet systems to determine how to avoid phenomena that disturb stable fluidisation flow. The specific air flow rate and pressure - needed for a given height and material solid-gas fluidised bed - were measured. The air flow rate versus bed resultant density functions and the settling velocity of given scrap particles in solid-gas fluidised beds of given density were also measured. Based on the lab-scale examination a pilot-scale separator was designed and built. Fundamental research with the pilot scale machine was carried out and after that the industrial size separator was designed and built. Fundamental applied research with the industrial scale machine was carried out with aluminium–copper scraps.

2. MATERIALS AND METHODS

The research work described in the article was largely carried out with equipment created by the authors; this section presents three such tools.

2.1 Laboratory-scale test equipment

Figure 2 shows a photo of the developed laboratory scale test equipment (A=0.025 m^2 effective separator cross section). The air was supplied by a compressor in the laboratory. The pressure was first regulated by a dedicated pressure regulator valve (1). This static pressure plays a key role because the downstream fluidised bed and the technical air distribution system represent a given flow resistance and that determines how much energy is consumed, namely what air flow rate will be developed in the common operating point.

The air flow rate was measured indirectly by a Venturi tube (2) and a differential pressure meter (3). The lab-scale fluidised bed separator (4) had two parts, the bottom, and the top. The air distribution system was built into the bottom part. Many different systems were tested to reach stable fluidising conditions. The top part was made with transparent walls to allow us to observe flow disturbances.

2.2 Pilot-scale separator

Figure 3 shows two photographs of the pilot-scale aero-suspension dense media separator. The left -hand photo shows the side view and the right-hand photo shows the top view of the machine.

The machine is an aero-suspension dense media separator with an endless chain to discharge the separated products. A similar design was made by the China University of Mining and Technology in 1994 (Sahu, 2009; He et al., 2016). The so called CUMT separator was installed and operated in a coal mine of Qitaihe Coal Co. for dry coal upgrading. Figure 4 shows the schematic drawing of the chain system with 6 rollers. The 6 bearings of the chain routing rollers can be well seen on the left-hand side of Figure 3. The Venturi tube with a differential pressure meter and the air distribution head are also shown. Effective cross-sectional area of the bed is 0.146 m^2. The pilot-scale device was loaded with zirconium-oxide media, as shown on the right-hand side of Figure 3.

2.3 Industrial-size machine

Figure 4 shows the schematic drawing of the industrial scale aero-suspension dense media separator (the effec-

FIGURE 2: Laboratory scale test equipment (1 pressure regulator, 2 Venturi tube, 3 differential pressure meter, 4 laboratory model fluidised bed reactor).

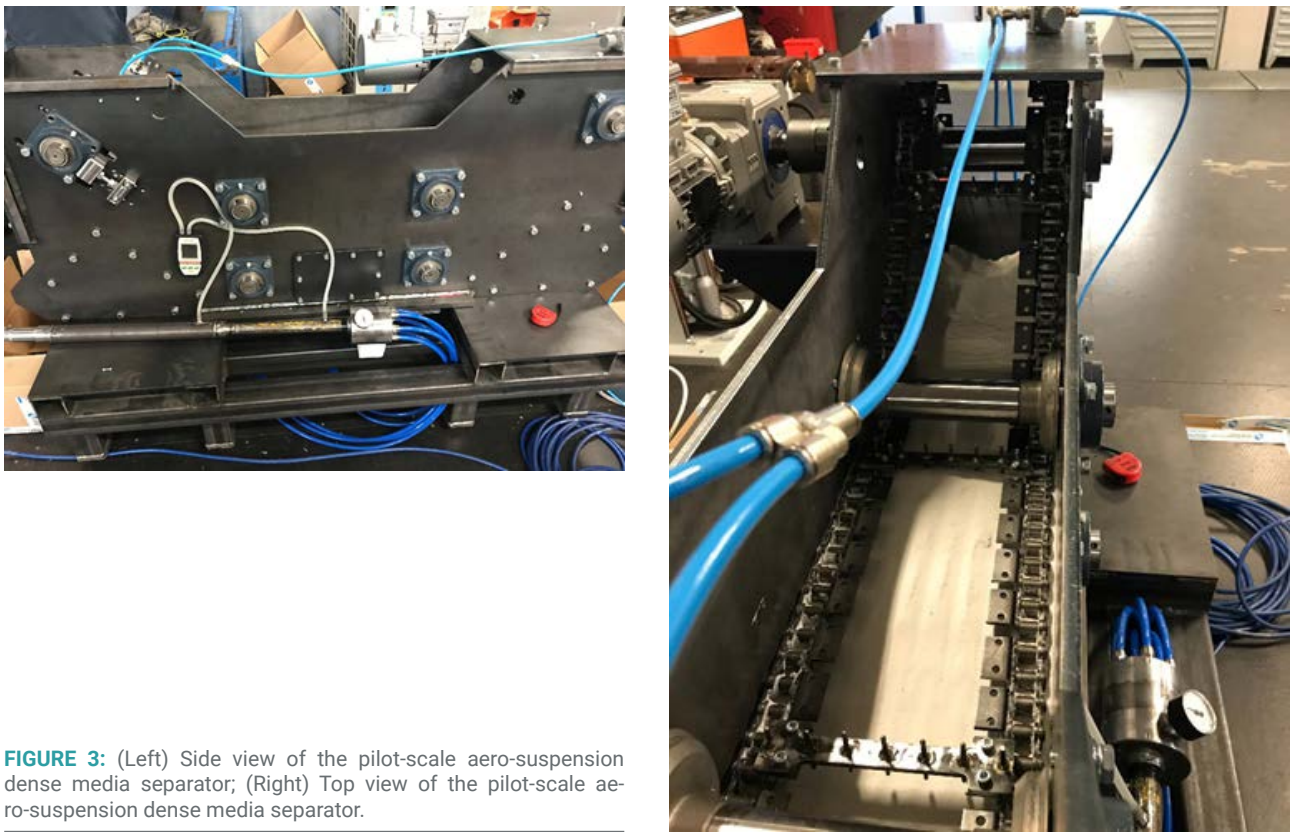

FIGURE 3: (Left) Side view of the pilot-scale aero-suspension dense media separator; (Right) Top view of the pilot-scale aero-suspension dense media separator.

tive cross-sectional area of the bed is 0.291 m^2). The mechanical engineering design of this machine was made by the Institute of Machine Tools and Mechatronics of the University of Miskolc. The machine has a massive steel frame. The frame is necessary to withstand the load because of the moving chain and comb elements of the discharge system in the fluidised bed. The discharge chain should work in non-fluidised separation medium as well. There are two endless chains at the front and back sides of the machine and cross-sectional combs are installed between them to discharge products. There are two toothed wheels and four non-toothed rollers. One toothed wheel is driven.

The centre part of the machine is charged with the bulk separation medium. The level of medium charge is higher than the level of the upper horizontal chain section, but it is lower than the product discharge points. The air is supplied by a compressor because the inlet pressure should be higher than 1 bar. There are built-in mechanical and air nozzle cleaning parts to clean the chains from the particles of the separation medium. The machine is modular; the width can be modified by changing the depth parts of it. Figure 8 shows a photo about the industrial scale machine.

2.4 Powder rheometer

The fluidisation behaviour of the different types of dense media was investigated in a Freeman Technology FT4 powder rheometer. During the measurements an air speed of up to 160 mm/s was used in a 25 mm measure-

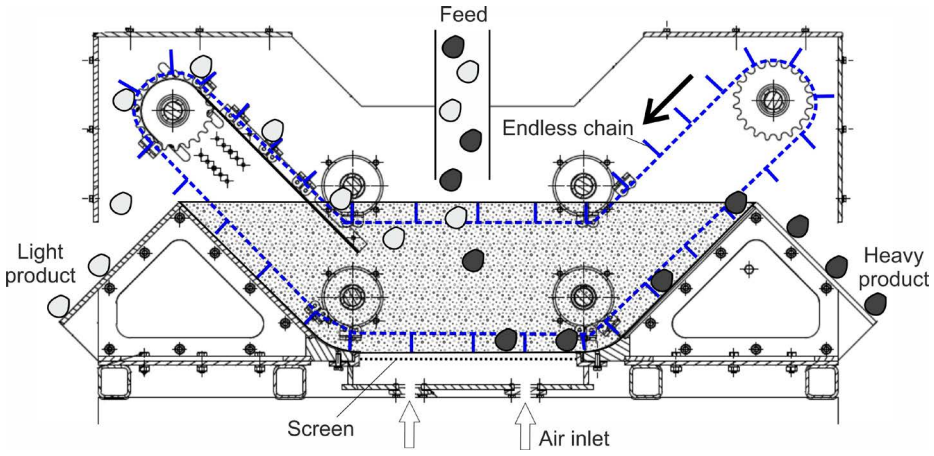

FIGURE 4: Schematic drawing and operational principal of the industrial-scale aero-suspension dense media separator.

ment cell to fluidise the material. These parameters were determined by preliminary tests. The total energy consumption for the rotation of a rotated paddle mixer (helix angle -5°) in the fluidised material was measured. The tip speed of the paddle was 80 mm/s.

2.5 Materials

Iron-oxide and zirconium-oxide powders were tested as working media during the development. The selection criterion of these materials was their high densities, because only with the application of high-density bed material can aero-suspension of suitable density be made. Different particle size fractions were made by manual laboratory sieving with a standard 200 mm laboratory sieve series. The size fractions were as follows in the case of iron powder: 0–100, 100–160, 160–200, 200–250, 250–315 and 315–400 µm.

The 160–400 µm iron powder size fraction was used for the laboratory scale fluidisation experiments and all others for the powder rheometer testing. The particle density of this fraction was measured many times in laboratory pycnometers; the average particle density was 6820 kg/m^3. The bulk density was measured by a volume calibrated glass cylinder; the average bulk density was 3085 kg/m^3. The porosity of the loosened bulk state iron powder fraction was ε_{mf}=0.548 (volume of air/volume of bulk). The mean shape factor of this used iron powder size fraction was determined by an optical microscope and image analysis (Φ=1.9; Figure 5).

Another material, zirconium-oxide, was also used for the laboratory-, pilot- and industrial- scale tests. The particle density of the 200–300 µm size fraction was 6060 kg/m^3 and the loosened bulk density was 3600 kg/m^3. The particle shape of zirconium-oxide can be considered spherical, according to image analysis (Φ=1; Figure 6).

The firm Inter-metal Ltd. collects mixed metal scrap from the area of Pest County, Hungary. The bigger metal pieces are cut by a guillotine shear as pre-shredding. Magnetisable particles are separated by a magnetic separator and fine particles are classified by sieving. The oversize product (30–100 mm) of the sieve goes into an eddy-current separator and its products are the useful conductive and the non-conductive contamination waste streams. The conductive product typically contains mainly aluminium and some copper. Without the aluminium–copper separation the value of this recycled metal is rather limited and this is the current challenge for the company. Samples were taken from the conductive product and one sample is shown on the left-hand side of Figure 9, used for the pilot-scale experiment described in Section 3.

3. RESULTS AND DISCUSSION

To understand the behaviour of the separation medium on the separation, fluidisation experiments were performed in a powder rheometer with iron powder and zirconia. The iron powder was divided into narrow particle size fractions and the measurements were performed with the size fractions given in Section 2.5. In the case of zirconia, balls with a nearly perfect spherical shape and very low surface roughness were used. Figure 7 shows the results of the fluidisation tests, where the total energy consumption to rotate a rotated paddle mixer with the same speed and path length in the fluidised material is presented. This total energy requirement was used to represent the effect of the air speed applied for the fluidisation of the material, and to evaluate the effect of the particle size and media type on the fluidisation of the media. For the 0–100, 100–160 and 160–200 µm fractions of the iron powder, as well as in the case of the zirconia balls (200–300 µm), the liquid-like behavioural state was reached, since the energy required to rotate the mixer stabilised as a function of the air velocity. For the coarser iron powder fractions, the air velocity was proved to be too low to achieve liquid-like behaviour. Mixing the iron powder without air velocity required much more energy than was required for zirconia balls, which can be explained by the spherical shape and smooth surface of the zirconia balls. For the different fractions of the iron powder, 160–200 mJ of total energy was measured without the use of air, while for the zirconia balls it was only 30–40 mJ.

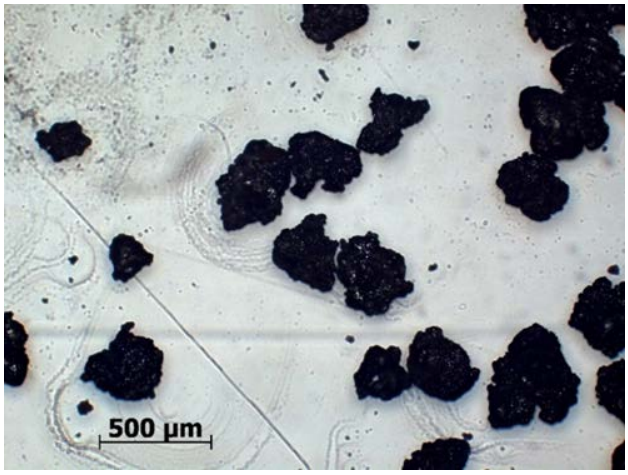

FIGURE 5: Particle shape of iron powder taken by an optical microscope.

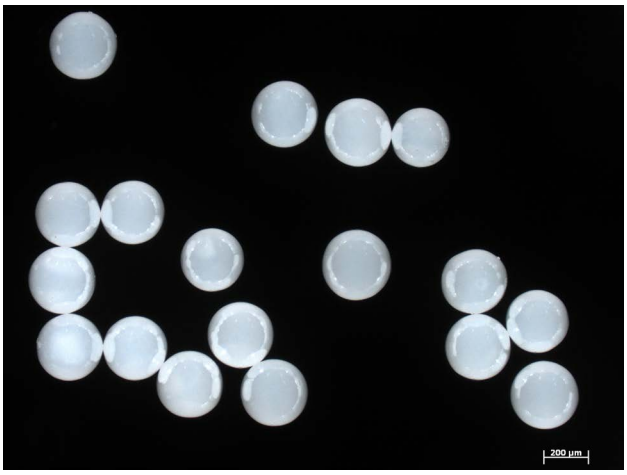

FIGURE 6: Particle shape of zirconia taken by an optical microscope.

This is of great importance in the design of the mechanical material discharger of the separator, as a much lower power drive chain may be required using the zirconia balls. As a result of the fluidisation, in the case of iron powder, the energy required to rotate the mixer was reduced by 30–50 times compared to the initial state.

If we examine the necessary air velocity for the liquid-like behaviour for each fraction, we can see that with the maximum particle size of the fraction, the required air velocity increases linearly in the case of iron powder. In the case of the zirconia balls, liquid-like behaviour was achieved at an air velocity lower than that of the iron powder compared to its particle size. Based on the performed tests, the separation medium should be as narrowly distributed in size as possible to be able to accurately adjust the air velocity required to reach the fluid state. The separation medium should have the smallest but still suitable particle size, because in this case a significantly lower air velocity is necessary for the fluidisation, which determines the required air flow. A medium with spherical particle shape seems to be more advantageous, as much less energy will be required to operate the separator.

Preliminary experimental series were carried out with the lab-scale test rig shown in Figure 2. Various quantities (m) of 160–400 µm iron powder were placed in the equipment and the non-fluidised height (H_{nf}) of the charge was measured first. Then the spring valve of the pressure regulator was gradually opened to a given point to set the regulated pressure after the regulator. Fluidisation conditions of the charge were visually observed. If the regulated pressure was too low, and therefore the air flow was too low, insufficient fluidisation took place. Increasing the pressure firstly resulted in good fluidisation conditions, while further increase led to increasingly high dust formation above the charged bed. The condition of the fluidised bed was manually checked by some aluminium and copper scrap particles hanging on wires. The surface of the fluidised bed looked like boiling water; many times, bubbles were randomly released. Figure 8 shows the industrial machine filled with zirconium-oxide charge and a bubble is clearly visible. Even though – on the surface – bubbling and dusting phenomena were not constant, the average height of this "bubbling zone" was also measured. A level increase of the charge in the reactor was not observable, only a bubbling zone developed above the material bed. Table 1 shows the measured results.

Results shown in Table 1 highlighted a design problem with the lab-scale test device, namely that the air velocity was too high in the air supply tubing, and therefore this pipe system was modified afterward. Pressure loss of the small tubing air supply was significant compared to that of the fluidised bed. Based on the results of the lab-scale tests the pilot-scale machine (Figure 3) was designed and built. Systematic fluidised bed fundamental and separation experiments were carried out. One of the aims of these tests was to determine the air supply requirements for the industrial size machine. The charge was filled into the 0.146 m^2 effective surface area pilot-scale machine at a non-fluidised height of 30 cm and the pressure regulator was set to 0.26; 0.38 and 0.4 bar-s. The measured air flow rates were 121; 148.7 and 159 m^3/h respectively. Although the set regulator pressure differences were relatively small, totally different fluidisation conditions were achieved: non-sufficient fluidisation for the smallest pressure, good fluidisation with slight air breakthrough for the medium and unacceptable air breakthrough for the highest was observed. For the air flow rate measurements a Venturi tube was used. The diameter of the smaller Venturi

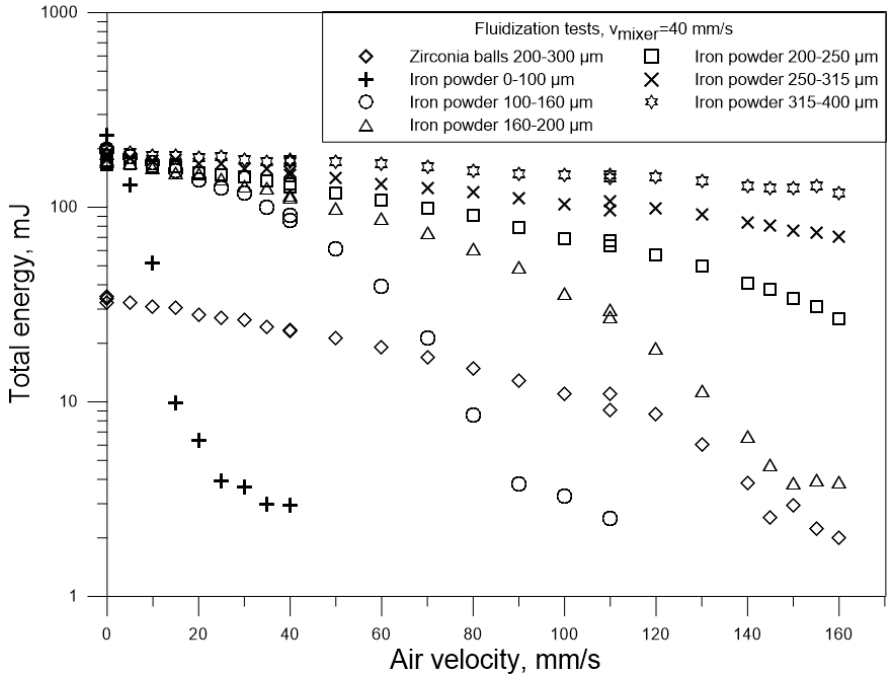

FIGURE 7: Fluidisation test results of the different media.

TABLE 1: Results of preliminary experiments carried out with the lab-scale test rig.

No. 1.	**mass of charge, m = 8 kg; non-fluidised height, H_{nf} = 11 cm;**				
Regulated pressure after the regulator [bar]	1	1.5	2	2.5	3
Height of bubbling zone [cm]	2	3	4	5	6
Air velocity in the 21 mm supply tube [m/s]	87.6	101.6	110.2	119.7	127.5
Condition	Not working	Not working	Not working	Not working	Not working
No. 2.	**mass of charge, m = 12 kg; non-fluidised height, H_{nf} = 15 cm;**				
Regulated pressure after the regulator [bar]	1	**1.5**	2	2.5	3
Height of bubbling zone [cm]	0	**3**	4	6.5	8.5
Air velocity in the 21 mm supply tube [m/s]	92.4	**105.4**	114.9	123.9	129.5
Condition	Not working	**Good**	High dust	High dust	High dust
No. 3.	**mass of charge, m = 16 kg; non-fluidised height, H_{nf} = 16.5 cm;**				
Regulated pressure after the regulator [bar]	1	**1.5**	2	2.5	3
Height of bubbling zone [cm]	0	**2**	4	6	8
Air velocity in the 21 mm supply tube [m/s]	87.6	**101.4**	111.3	120.5	134.7
Condition	Not working	**Good**	High dust	High dust	High dust

pipe section was 0.027 m and that of the bigger pipe section was 0.04 m. When good fluidisation was taking place the pressure loss on the Venturi tube was 1700 Pa, which corresponds to 148.7 m^3/h air flow rate and 1021 m^3/m^2h specific air need for the pilot-scale separator. On the basis of the results of the pilot-scale tests the industrial machine (Figure 8) was designed and built. Systematic fluidised bed separation experiments were carried out.

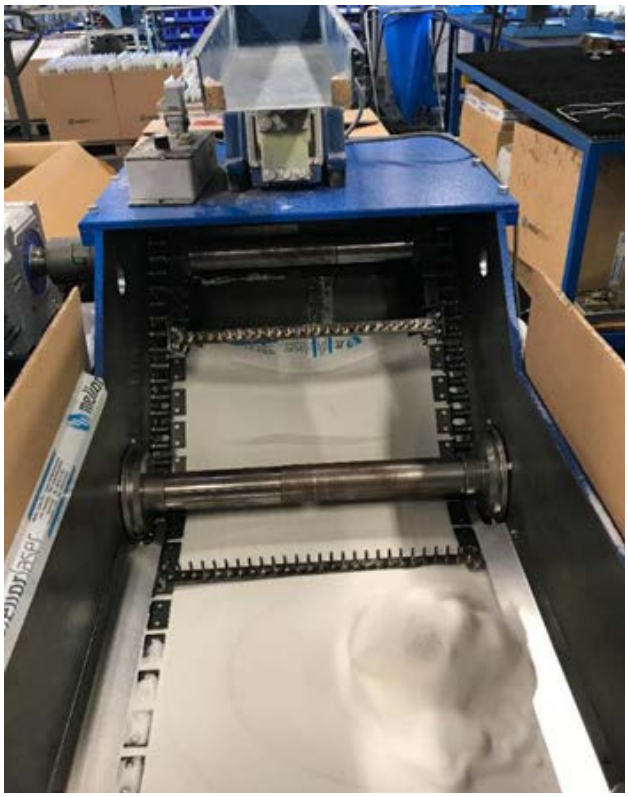

FIGURE 8: Photograph of the industrial-size aero-suspension separator.

Results of one test are shown here just as an example (Figure 9 left and right). Five kg of material was evenly fed to the equipment by a vibrated feeder for 60 seconds (Figure 9 left). Mass flow rate of feed was m_F = 300 kg/h. The copper-aluminium scrap sample is shown on the right-hand side of Figure 8. Mass yield of the Al product was g_{Al} = 81.25% and e_{Al} = 84.23% of the Al and e_{Cu} = 0% of the Cu in the feed was recovered to the Al product. Mass yield of the Cu product was g_{Cu} = 18.75% and e_{Al} = 15.77% of the Al and e_{Cu} = 100.0% of the Cu in the feed was recovered to the Cu product. 270 g of aluminium remained in the equipment. However, if the machine operates continuously, this remaining material is also discharged from the equipment. The Al product was pure a_{Al} = 100% aluminium, but the Cu product was not clean, it contained some aluminium. These incorrectly separated Al particles were probably discharged to the Cu product in two different ways: (1) an Al particle was stuck to the combs, travelled through the fluidised bed by the chain and then fell out on the Cu side; or (2) on the Cu side a dead space (non-fluidised separation medium) was formed and an Al particle which was trapped in this volume was discharged on the Cu side. Flat aluminium particles are difficult for the combs to handle. At discharge, flat particles may slip back into the separation space under the teeth of the combs (this was the reason for the 270 g of residual aluminium). Certain crumpled aluminium particles stick to the teeth of the combs, even very tightly, and the combs can make several turns with them. By installing more than one comb, the combs would be subjected to a lower load, so the capacity would be increased. The different magnitude tests that were carried out are a good basis to improve process engineering design methods of aero-suspension dense media separation. Table 2 summarises the main technical parameters of the laboratory, pilot and industrial scale machines and experiments.

The theoretical minimum differential pressure (Δp) that can provide enough hydrodynamic force to lift the particles

FIGURE 9: (Left) Feed of pilot experiment (30–100 mm copper-aluminium scrap); (Right) Products of pilot experiment (Al and Cu products).

of a given load of separation medium in a bed can be calculated from Eq. 2. Then the minimum fluidisation velocity (V_{mf}) can be calculated from the Ergun equation (Eq. 1). The quadratic Ergun equation was not solved analytically; instead, the positive solution of V_{mf} was iteratively calculated by Microsoft Excel. The earlier defined Reynolds number describing the air flow through the pores of the fluidised separation medium was calculated by Eq. 3. Results are shown in Table 3. The development and size upgrading of the different separators were based on the measured specific air need for sufficient fluidisation of a given separation medium charge. A theoretical specific air need value can also be calculated by Eq. 4. The minimum fluidisation velocity is the velocity of air through the pores, therefore, if this velocity is multiplied by a unit cross section (A_u) and divided by the porosity, the result is the specific air need (Q_s) for the given height of separation medium charge and machine.

$$Q_S = \frac{V_{mf} \cdot A_u}{\varepsilon_{mf}} \quad (4)$$

The height of the iron powder load in the laboratory separator is almost half that of the zirconium-oxide charge in the pilot-scale and industrial equipment, but the necessary minimum fluidisation velocity is much higher. This result

TABLE 2: Summary of different test data.

Test	Separation medium	Separator
LAB	iron powder d_p=280 µm; ρ_p=6820 kg/m^3; ε_{mf}=0.548; Φ=1.9	laboratory scale separator (Fig. 2) A=0.025 m^2; H_{mf}=0.165 m; m=16 kg
PILOT	zirconium-oxide d_p=250 µm; ρ_p=6060 kg/m^3; ε_{mf}=0.406; Φ=1	pilot scale separator (Fig. 3) A=0.146 m^2; H_{mf}=0.3 m; m=158 kg
IND	zirconium-oxide d_p=250 µm; ρ_p=6060 kg/m^3; ε_{mf}=0.406; Φ=1	industrial scale separator (Fig. 8) A=0.291 m^2; H_{mf}=0.3 m; m=315 kg

TABLE 3: Measured and calculated main technical parameters for laboratory-, pilot- and industrial-scale equipment.

		Calculated				Measured	
Test	H_{mf} [m]	V_{mf} [m/s]	Re_{mf} [-]	Δp [bar]	Q_s [m³/m²h]	p [bar]	Q_s [m³/m²h]
LAB	0.165	0.886	31.44	0.031	5823	1.5	5057
PILOT	0.3	0.148	2.47	0.106	1313	0.38	1021
IND	0.3	0.148	2.47	0.106	1313	0.38	1021

is in good correlation with the powder rheometer tests, indicating that the particle shape of iron powder is not spherical, and its surface is not smooth. The industrial size separator is a wider machine than the pilot-scale version; therefore, all of their calculated and measured specific data in Table 3 are identical. The difference is in the mass of the separation medium charge and in the separator surface. The calculated theoretical minimum differential pressure is significantly lower than the measured pressure after the regulator valve. In the case of the laboratory separator, it is much smaller. This indicates an initial insufficient machine design because the head pressure after the regulator valve supplies all the flow losses of the connecting pipes, the air distribution system and most importantly the drilled holes in the distribution pipe sections. Too small diameters of structural components of the laboratory separator were used. Although the necessary quantity and pressure of air were supplied for the fluidisation, the auxiliary losses were too high. The specific air need values measured and calculated (by Eq. 4) are very similar. This indicates that the Ergun equation can be used for the process engineering design of aero-suspension dense media separation. If the material properties of the separation medium are known, the air need for a given height separation medium load can be estimated by Eq. 4 using the Ergun minimum fluidisation velocity. The head pressure of the air supply system must be higher than the calculated minimum value. The calculation of the head loss of the air supply and distribution system can be determined by standard fluid dynamics calculations. This means that using the presented method, an aero-suspension dense media separator can be designed by just knowing the material features without any tests. This developed and validated process engineering design method of gas-solid fluidised bed separators can be used by both academia and industry.

4. CONCLUSIONS

A laboratory scale fluidised bed separator was built and charged with different granular materials to study fluidisation. A pressure regulator can be applied and by opening its spring valve up to a given point, a steady-state air flow rate can be set. If the air supply was low the charged bed was not fluidised. There was only a very narrow air flow rate range within which a good fluidised bed was formed. In this narrow range, the surface of the charged bed started to “boil”, forming bubbles. Al particles floated and Cu particles settled in this good fluidised bed. If the air flow rate was further increased, bubbling increased and dust was released, and the operational conditions were no longer appropriate.

Different size fractions of iron powder and zirconium-oxide were tested in a powder rheometer. Mixing the iron powder without air fluidisation required much more energy compared to mixing zirconia balls, which can be explained by the spherical shape and smooth surface of the zirconia balls. The fluidised powder rheological tests resulted in much lower driving energy for the zirconia balls. As a general conclusion a narrower particle size distribution of the separation medium is better because fluidisation is easier and spherical shape and smooth surface are better because of the lower mixing (fluidisation) energy need. Based on the results of the lab-scale tests a pilot-scale and later an industrial scale machine (400 kg/h) were designed and built. Separation experiments were carried out with aluminium-copper scrap in the 30–100 mm particle size range. This is a limitation of the machine, because only this size range can be separated with this machine. The Al products were typically clean, but the Cu products contained some aluminium contamination. For the Cu product a secondary separation step might be necessary to produce pure copper. The Ergun model was used to calculate the minimum pressure difference and fluidisation air velocity for separation experiments with iron powder and zirconia at the scale of the laboratory, pilot and industrial-size equipment. It is concluded that the specific air need of a given type and height separation medium machine can be calculated by the Ergun model, because the measured and calculated values are in good agreement. The measured pressures after the air supply regulator valves were higher than the calculated Ergun minimum differential pressures because the air supply system covers the flow losses of the pipes, air distribution system and also the drilled holes of the distribution pipe sections. When the machine design is proper these auxiliary losses are low but cannot be zero.

In addition to the machine development, the developed process engineering design method on the basis of the newly introduced specific air need for a given height of separation medium charge parameter for gas-solid fluidised bed separators has the advantage, that – even without building the machine – the technical parameters can be calculated just on the basis of results of simple material testing.

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FAST FASHION VERSUS CIRCULAR ECONOMY: AN EXCITING MATCH?

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ABSTRACT

Fast Fashion is an extremely successful business model that brings apparel and home textiles to the market in ever shorter lead times at ever lower prices. On the one hand, this can be seen as extremely consumer-friendly, as customers can afford top-styled clothing that is always in line with the latest trends, even on a small budget. The opportunity to dress fashionably therefore does not remain a privilege of high earners. On the other hand, the production of fast fashion takes place without compliance with social and environmental standards. It's all about producing as cheaply and quickly as possible. In the EU, the linear economic model is currently being transformed into a circular one. This development does not stop at the textile sector. The textile industry is obliged to bring more durable products onto the market, to comply with social and environmental standards, and to recycle a high proportion of the textiles at the end of their life cycle. In this communication it is shown that fast fashion leads to an uncontrolled growth of textile production and that recycling alone cannot be the solution. The only way is to tackle the problem at its roots and not to regard waste prevention as just an empty phrase. It is obvious that fast fashion and the circular economy are not compatible and that there can only be one winner.

1. INTRODUCTION

1.1 The textile production chain

The manufacture of apparel or other textiles requires a multi-step process that is globally dislocated. In contrast to packaging, the textile processing chain is much longer and thus the consumption of resources and energy is very high. Table 1 summarizes the energy demand for the production of apparel broken down according to the individual process steps.

Therefore, according to literature the energy consumption over the entire textile processing chain can add up to 960 GJ/t (Steinberger et al., 2009). The broad range is due to the fact that the (secondary) spinning and weaving or knitting steps, in particular, are strongly dependent on the type of yarn (especially yarn titer) or fabric (especially grammage).

Due to the length of the textile processing chain numerous opportunities to close loops are possible. In addition to reuse (i.e., second-hand clothing), recycling can occur at the fabric, fiber, polymer, or monomer level. Naturally, the less one has to go back in the textile processing chain, the greater the savings potential. However, it must be taken into account that there are certain limitations that prevent short cycles, such as blends of different polymers or the presence of impurities. For recycling, it will be necessary to

TABLE 1: Cumulative energy demand for the production of textiles (Roithner et al., 2021).

Process step	Cumulative energy demand / GJ/t	Remark
Raw material production	PET: 69 – 81 PA: 119 - 129	Only man-made fibers
Fiber production	Cotton: 55 - 69 PET: 89 - 110	Cotton: high water consumption (up to 24,000 m³/t), energy (fossil-based), agrochemicals
Yarn formation	95 - 190	Strongly dependent on titer
Fabric formation	100 - 310	Strongly dependent on grammage
Wet processing	104 - 398	Large quantities of waste water
Cutting / sewing	105 - 420	

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use all available processes, even down to the monomer level, and to choose the combination that offers the greatest ecological and economic advantage.

1.2 The fast fashion business model

In the apparel industry, the term "fast fashion" has become increasingly important in recent years. "Fast fashion" refers to a business model in which textiles are put on the market in short cycles, offered cheaply and without a long shelf life. Garments are designed, produced and put into stores as quickly as possible to match the latest fashion style. The main characteristic is the shortening of the time to market. This leads to a rapid change of collections and ultimately to an unsustainable and increased consumption of resources. At the same time, sales are boosted.

Figure 1 shows the sales of the leading fast fashion brands in 2021 and 2022. Inditex, which comprises brands such as Zara, Bershka, Massimo Dutti, Oysho, Pull&Bear, Stradivarius, Uterqüe and Lefties is the largest player and is accounting for just over a quarter of sales (32.6 bn€ in 2022). However, Shein has almost doubled its sales from 2021 (14.7 bn€) to 2022 (28.1 bn€) and is close on the heels of Zara (Statista, 2023c). Shein is a Chinese company that has once again accelerated the fast fashion business model, completely ignoring environmental protection and ethical principles (Bottini, 2022).

A close look at the company Inditex reveals that the sales have increased almost sixfold from 2004 (5.6 bn€) to 2022 (32.6 bn€). Even though there was a 28% drop in 2020 due to the pandemic, the average CAGR in this period was 11%, which corresponds to a doubling time of only 6.6 years (see Figure 2).

An end to the rapid growth does not seem to be in sight. As shown in Figure 3, the sales of companies in the fast fashion sector are expected to double again in just six

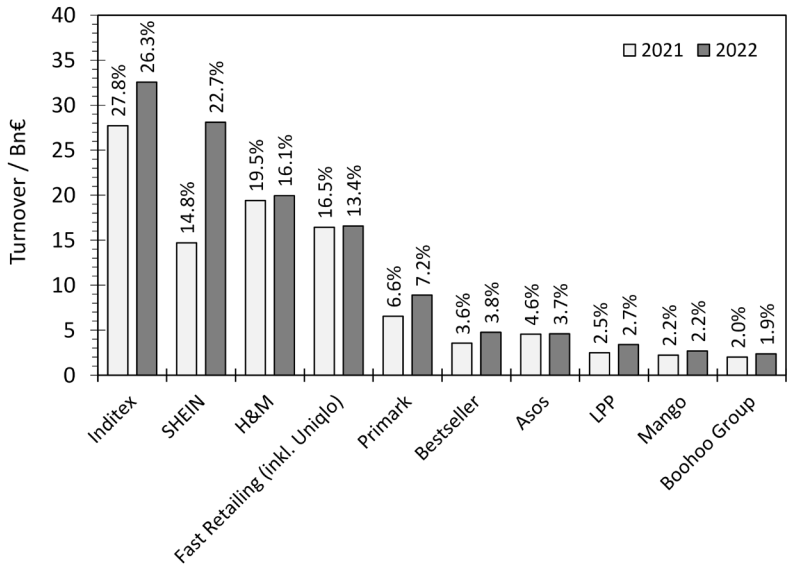

FIGURE 1: Sales of leading fast fashion groups worldwide in 2021 and 2022. The percentages refer to the market share of the respective fashion groups (Statista, 2023c).

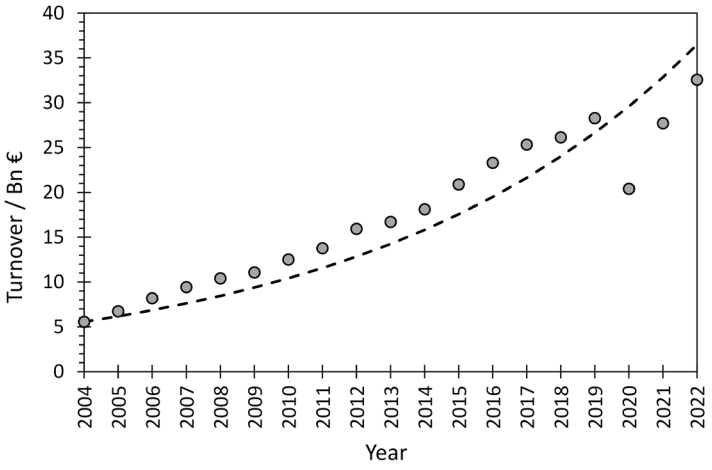

FIGURE 2: Inditex Group's sales worldwide from 2004 to 2022 (Statista, 2023b). The dashed line indicates an annual growth rate of 11% based on 2004.

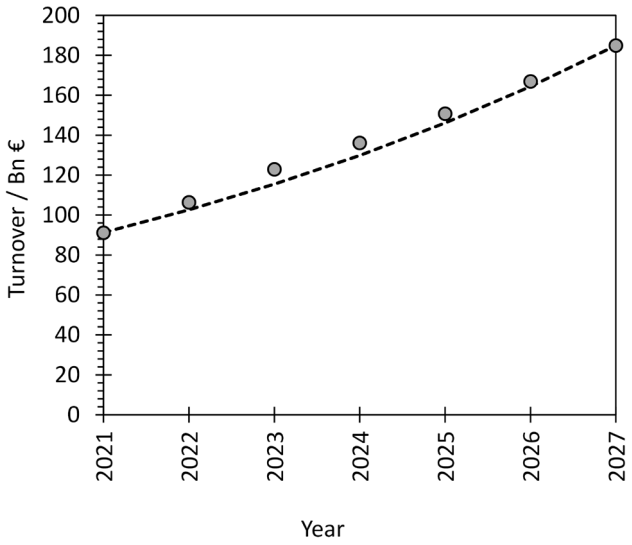

FIGURE 3: Outlook on sales of leading fast fashion groups from 2021 to 2027 (Statista, 2023a). The dashed line indicates an annual growth rate of 12.5% from 2021.

years (from 2021 to 2027) which corresponds to an annual growth rate of 12.5% (Statista, 2023a).

1.3 Circular economy in the EU

In recent years, the European Union has set a goal to transform our current linear economic model into a circular one. Circular economy is understood as a regenerative system in which resource consumption and waste production are minimized by closing energy and material cycles (Commission, 2015). Typically, sustainable design, maintenance, repair, reuse, re-manufacturing, refurbishing and recycling are proven means to achieve this goal. Due to the amendment of the waste framework directive (WFD) in 2018 (Commission, 2018), textiles are also included in the circular economy concept. The EU Commission expects the transition to a circular economy not only to reduce environmental impacts, but also to improve the security of supply of raw materials and have a positive impact on employment in the EU.

The Commission's focus on textiles is reflected not least in the fact that, in addition to the implementation of textiles in the WFD, other documents that are wholly or at least partly related to textiles have been published, such as the Circular Economy Action Plan in 2020 (Commission, 2020), the EU Strategy for Textiles in 2021 (Commission, 2021) and the EU Strategy for Sustainable and Circular Textiles in 2022 (Commission, 2022). Only recently, on 5 July 2023, the commission has made a proposal for an amendment of the WFD (Commission, 2023a). This document also includes Annex IVc, which defines which textile, textile-related and footwear products will fall within the scope of the foreseen extended producer responsibility. The Commission has clearly stated that it is committed to moving the textile industry towards a circular economy.

TABLE 2: Global (recycled) fiber market in 2021 by fiber type (Exchange, 2022).

Fiber type	Production volume	Market share of recycled fibers	
	10^6 t	wt%	10^6 t
PET	72.2	15*	10.8*
WO	1.0	6	0.06
EL	1.2	3	0.04
PA	5.9	2	0.12
CO	24.7	1	0.25
MMCF	7.2	0.5	0.04
PP	3.0	0.2	0.01

** derived practically exclusively from PET bottles*

2. GROWTH VERSUS RECYCLING

In a superficial view, it could be concluded that fast fashion in combination with circular economy can form an excellent symbiosis. Through the business model of fast fashion, people can be supplied with affordable fashion. Parallel to this, recycling (of textiles) is included in the EU Circular Economy Package and could help reduce the textile industry's need for primary raw materials (polymers). In addition, textile recycling could create new "green jobs".

Already, Inditex, for example, is making efforts to meet energy consumption from renewable sources, to use sustainably produced cotton, and to use polyester made from recycled materials. The company claims in its 2022 annual report (Inditex, 2023) that the following goals, among others, have been achieved or will soon be achieved:

- use of 100% renewable electricity at its own facilities;
- use of preferred fibres in its products (100% cotton and cellulosic fibers in 2023 and 100% polyester and linen in 2025;
- 25% reduction in water consumption in the supply chain by 2025.

Only recently it has been shown that companies following the fast fashion business model have launched activities to achieve SDG's. However, in fact, brands tend to do "business as usual" and increase greenwashing activities instead (Garcia-Ortega et al., 2023). Finally, large players in the fast fashion sector still rely on driving sales numbers up. Many customers do not understand the negative impact of excessive (textile) consumption on the environment (Hugo et al., 2021). It is therefore still a long way to move fast fashion in the direction of Circular Economy.

Currently, fiber-to-fiber recycling is virtually non-existent. As demonstrated in Table 2, at first glance, it appears that PET fibers have a relatively high recycling rate, as they are made from 15% recycled material (Exchange, 2022). However, recycled PET is derived almost exclusively from PET bottles and fiber-to-fiber recycling is essentially zero. Of the other fiber types, wool has the highest recycling rate at 6%, although with an annual production of around 1 million t, only 60,000 t of fibers are recycled. From this perspective, although the recycling rate is only about 1%,

cotton is in the lead in recycling with a quarter of a million tons. In total, well under 1 million t of fibers are thus actually sourced from textile waste.

It is undisputed that recycling is an effective means of reducing the need for native raw materials. Even though recycling in the textile sector will gain importance based on the new legal framework, the massive growth driven by the fast fashion business model must also be taken into account. The production volume of synthetic polymer fibers has grown by an average of 5.6% annually from 1970 (4.8 million t) to 2022 (72.2 million t) (CIRFS, 2020; Exchange, 2022). This corresponds to a doubling time of 12.7 years. While such growth may be a benefit to the economy, it will not be sustainable for the environment in the long run (Bartl, 2020). If this growth continues in the next few years, the production volume will reach 140 million t by as early as 2032, about twice the volume of 2020. In 2038, the production volume of synthetic polymer fibers would even reach 200 million t, which is about twice the total fiber market in 2020.

Assuming optimistically for the year 2032, that 50% of synthetic polymer fibers are sourced from textile recycling (i.e., direct fiber recycling or produced from the recycled fiber polymer, that would be 71 million t), the demand for virgin polymers would be more or less equal to today's high demand (69 and 71 million t, respectively) as sketched in Figure 4. If we further assume an even more ambitious increase of recycled material content, due to technological progress and stringent legislation, from 50% in 2032 to 66% by 2038, this would reflect deriving an ambitious 129 million t of synthetic fibers from end-of-life textiles (see Figure 4). However, the demand for native raw materials for fiber production would still only decrease insignificantly (from 69 to 67 million t).

Hence, while recycling is indeed a necessary must in the textile sector, it is not sufficient at all. Even if textile recycling is a suitable measure to reduce the consumption of primary resources, growth will compensate all technological progress.

3. CONCLUSIONS

Even if a high percentage of end-of-use textiles should be recycled due to the current stringent EU regulations, the business model of fast fashion always leads to a high consumption of resources along the textile processing chain. The above-mentioned limitations (Figure 4) only consider the demand for native material for polymer production. However, textile recycling requires going several steps back in the textile production chain and, to a certain extent, going through it again. Depending on the condition of the end-of-use textiles, they can be fed back into the process chain at different re-entry points (i.e. as fibers, polymers or monomers), which means that at least part of the process chain has to be run through again. This means that despite recycling, significant energy consumption and emissions, especially wastewater, have to be accepted (Ipsmiller & Bartl, 2022; Roithner et al., 2021). However, for this to be feasible, it should always be attempted to plan and implement necessary recycling technologies of the future in line with minimum design requirements. Decisions should be made in close coordination of legislation and technology owners and there needs to be a binding consensus on what is a minimum requirement to provide the necessary function of the textile (brands), what really needs to be avoided from a technological perspective (recyclers) and what the best compromise for that in terms of legal limitations could be.

Ultimately, recycling can only address the symptoms and not, as would be appropriate, the causes. To achieve a massive reduction in resource consumption, it is essential to reduce the amount of textiles sold. Probate means for this are for example an extension of the useful life ("design for durability"), reuse or alternative business models (e.g., leasing). The volume of second-hand clothing sold within the EU must be massively increased by accompanying measures such as repairing, re-manufacturing, re-purposing as well as consumer awareness.

All of these valuable strategies may not be implemented voluntarily, and if a consensus as mentioned above is

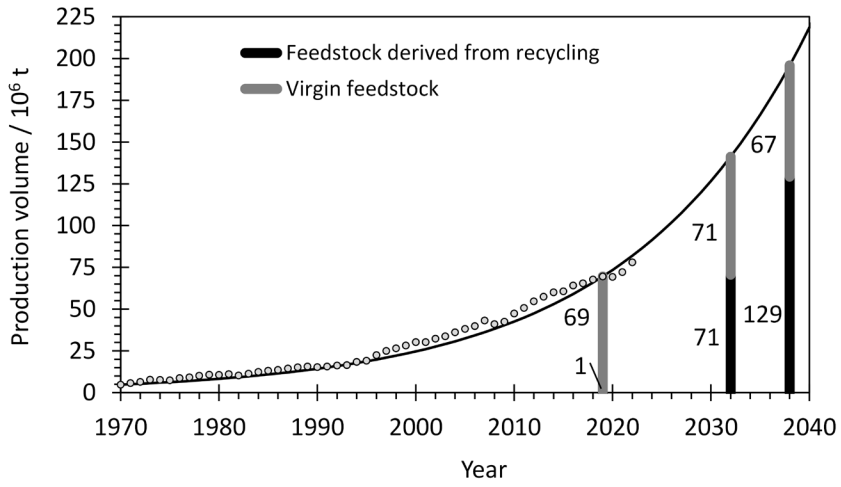

FIGURE 4: Production volume of synthetic fibers (circles) from 1970 to 2022 (CIRFS, 2020; Exchange, 2022). The curve indicates an annual growth rate of 5.6% from 1970. The black columns show the amount of fibers sourced from recycled material (fiber-to-fiber) and the gray columns show the amount of fibers derived from native resources (assumption: recycling rate in 2032 is 50%, in 2038 66%).

not found, this will then require massive legal regimes. Some of the Commission's proposals on textiles are actually correct, but there is no clear indication of how they are to be achieved. An EPR system, as proposed by the Commission, may shift costs from general waste charges to polluters (i.e. textile distributors), as shown for packaging waste, but it will not necessarily reduce the amount of waste (textiles) or make it easier to recycle. The collection rates that can be achieved by means of EPR are often too low, so the Commission is currently considering an EU-wide deposit system on single use plastic beverage bottles (Commission 2023b) and like it would also be a way for textiles to achieve an almost complete return rate. An exclusive treatment of textile waste in the EU could prevent negative impacts on the local textile processing chain in the recipient markets and also stop the disorderly dumping in these countries. Finally, (legally prescribed) higher prices for textiles would be a proven way to reduce the consumption of virgin apparel, thus to increase the attractiveness of second-hand clothes and to alleviate the pressure to export end-of-life clothes to developing countries. It is clear that these measures will be fiercely opposed by a large number of stakeholders such as industry, trade or consumers. It is therefore clear that the business model of fast fashion is not compatible with a circular economy. From this point of view, an exciting match between industry and legislation can be expected in the near future. In any case, keep your fingers crossed for the environment.

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ENHANCEMENT OF BIOGAS GENERATION BY UTILIZING RAW AND MODIFIED WITH HNO_3 BIOCHAR OBTAINED FROM PYROLYSIS OF BIOMASS AND DIGESTATE

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ABSTRACT

Biomass- and digestate-derived biochars were modified with nitric acid solution and examined in biochemical methane potential (BMP) tests to determine the effect of pretreatment on each of the different materials capability to improve the biogas production from the anaerobic digestion of conventional substrates such as corn silage. Methane yields from corn silage (0.308 $m^3kg_{VS}^{-1}$) were over the average value for the specific type of lignocellulosic material. Addition of digestate-derived biochar (BCD) in AD process improved the methane production 1.13-fold. However, the sawdust-derived biochar (BCS) resulted in an even greater methane release of 0.374 $m^3kg_{VS}^{-1}$. Chemical treatment reduced the pH of BCs from 10.29 and 11.54 to 3.10 and 2.81 for BCS and BCD, respectively while had a significant impact on materials composition almost removing the ash and metal elements from BCS and markedly decreasing 1.43-fold the ash fraction and by 70-75 % the minerals proportion in BCD. The presence of modified digestate-derived biochar (M-BCD) in a culture led to an enhanced methane production (0.402 m^3kgVS^{-1}) indicating that the specific additive exhibited a higher potential than all BCs to promote the efficiency of AD of a biomass feedstock. M-BCD also possessed the greatest capability to lessen an inhibition caused by H_2S retaining the concentration of the toxic gas at levels lower than 100 ppm. On the other hand, modified BCS provoked a 9% abatement in methane yields providing evidence that nitric acid could have a neutral or slightly negative effect on the capability of a BC to improve the AD process.

1. INTRODUCTION

Anaerobic digestion (AD) is the biochemical conversion of complex organic structures by microorganisms for the production of biogas in an anoxic environment. AD provides an efficient technology for the generation of renewable energy, however, faces a number of challenges including the low biodegradation efficiency, low by-products quality, long start-up times and system instability restricting its even broader application (Fagbohungbe et al., 2017). Various supporting materials such as nano-structured carbons and metals, biochar (BC), zeolites, and ore powders have been applied in AD systems to aid the process (Shen et al., 2020). BC, a carbon-rich material produced by pyrolysis of biomass, has been recognized as an AD additive capable to improve the process (Li et al., 2019; Pan et al., 2019; Salehiyoun et al., 2022) by functioning as (1) supporting media for the adhesion of microorganisms, (2) buffer for regulating system acidity, (3) adsorbent for controlling the concentration of inhibitory substances and (4) stimulator of methanogenesis assisting the direct interspecies electron transfer (DIET) (Fagbohungbe et al., 2017; Kobayashi and Kuramochi, 2022; Lü et al., 2016; Shen et al., 2020).

BCs produced from biomass have principally been reported to improve the efficiency of an AD system. Lü et al. (2016) who added fruitwood BCs (800-900°C) in a mesophilic digester noted that chars reduced the methanization lag phase by 6-24% and increased the methane production rate by 23.5-47.1%. Sunyoto et al. (2016) stated that a pine sawdust BC (650°C) enhanced the maximum production rate and yields of methane by 41.6 and 10%, respectively and concurrently shortened the lag phase of the AD of aqueous carbohydrates by 41%. Likewise, Salehiyoun et al. (2022) ascertained that a wood BC enhanced the rate and yields of methane (36.6%), controlled acidification and shortened the lag phase during AD of municipal solid waste (OFMSW).

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Apart from biomass, there are several different feedstocks that could be used for the production of BC. Digestate is a by-product of AD that could be transformed into BC since it retains major part of the properties of the primary material used as substrate in AD. Transformation of digestate to BC and its subsequent use as additive in AD could provide a series of environmental and economic benefits. In a recent report (Basinas et al., 2023), BC prepared from a digestate was found to have significantly different properties than a biomass char and it was anticipated that will present a different impact on the AD of lignocellulose. However, the application of digestate biochar as support for the AD of conventional substrates such as corn silage has attracted limited attention and little information on the effect of this type of material on the AD process can be found in the literature.

BC performance in AD is prominently defined by BC properties like porous structure and the presence on its surface of oxygenated functional groups such as C=O, OH, and COOH. Biomass-derived BC presents a surface functionality that could support AD due to a sufficient porosity and surface area as well as an existence in its structure of C–O, C=O, and OH groups (Liu et al., 2015). However, modification with chemical methods could further improve the properties related to the enhancement of AD efficiency, especially the porosity since chemical agents facilitate a generation of new pores by removing fractions of carbonaceous molecules from BC structure (Kobayashi and Kuramochi, 2022; Liu et al., 2015). Zhu et al. (2018) observed a major increase in the surface area of BC as a result of a treatment with potassium carbonate. In addition to porosity growth, oxygenated functional groups like -COOH and -OH are introduced into BC with oxidation which could also aid the enhancement of a substrate's conversion in an AD system (Li et al., 2014; Liu et al., 2015). Nitric acid has been recognized as one of the most efficient agents for BC modification (Liu et al. 2015). Vu et al. (2017) reported that the number of surface carboxyl and sodium-containing functional groups of corncob-derived BC increased after its modification with HNO_3 (6 M) and NaOH (0.3 M). This caused an increase in the surface adsorption capacity of the BC and a subsequent reduction of ammonia in the system. In any case, modification of biomass-derived BC aimed at improving the surface area, pore volume and surface functional groups of BC. The same treatment could also be of relevance to increase the pore volume and functional groups of a digestate-derived BC, however no information is available about the effect of a nitric acid treatment on the properties of a digestate BC. Moreover, the influence of chemical treatment on the capability of a digestate-derived char to catalyse the AD has not been considered yet.

In the present study, BCs produced from a typical biomass and a digestate obtained from a mesophilic agricultural biogas plant were subjected to chemical treatment with nitric acid and all the materials examined for their capability to improve the efficiency of the AD of corn silage. The target of the work was to evaluate the effect of digestate derived BC on the AD process and correlate it with the case of biomass chars. Another aim was to assess the efficiency of an AD process supported by an engineered biocarbon produced using digestate-derived BC and make comparisons with the performance of systems assisted by biomass and pretreated biomass BCs.

2. MATERIALS AND METHODS

2.1 Sample collection and biochar preparation

Two different type of materials were used for production of BC. A typical biomass (sawdust) and a digestate obtained from the first stage of a mesophilic agricultural biogas plant (Pustějov II-Zemspol Studénka Ltd) operating on wet mode at 40°C with a substrate consisted of corn silage and small proportion of cattle slurry were used for the production of BC. Both materials were dried at 105°C under inert conditions (N_2), milled (IKA Tube Mill Control) and sieved to a particle size fraction between 100-300 μm.

BCs were generated in a bench-scale pyrolysis reactor operated from atmospheric temperature to 800°C with a heating rate of 10°C/min and a constant pyrolysis time of 180 min. The custom-made reactor consisted of a vertically oriented stainless-steel tube (50 mm internal diameter) placed inside an electrically heated furnace whereas the setup contained tar collection and gas cleaning systems. BCs prepared from sawdust and digestate referred to as BCS and BCD. More details about the pyrolysis reactor and procedure followed can be found in Basinas et al. (2023).

Modification of BC was carried out by soaking 50 g of material in 500 mL of a 66%vol. nitric acid solution and heating the mixture at 81°C for a total of 6 h while it was stirred at 200 rpm (Gao et al., 2021). Modified BC was washed with deionized water three times, filtered and oven dried at 105°C for 24 h. The modified BC from BCS and BCD will be referred to as M-BCS and M-BCD, respectively.

2.2 Characterization of materials and biochars

The TS content of substrate and inoculum was determined in a KERN DLB 160 3A moisture analyser and VS content by estimating the loss on ignition of material in a LECO TGA 701 thermogravimetric analyser. The same analyser was used for the proximate analysis of BCs. The mineral composition of samples was determined using Atomic Absorption Spectroscopy (HR-CS AAS contrAA 700) after dissolving the solids in aqua regia according to EN 16174:2012 standard. A LECO Truspec CHN and S628 elemental analyser was employed for the determination of the elemental composition of samples. A WTW 340i pH-meter (SenTix 410 sensor) was used for pH measurements. Carbohydrates were determined according to the ASTM D5896-96 and proteins by titration according to EN ISO 5983:1997 standard method. All analyses were performed in duplicate.

A scanning electron microscope (SEM) (Tescan Vega) equipped with a Tungsten cathode and energy-dispersive X-ray spectroscope (EDS) was used to determine the texture of materials. Micrographs were obtained using a secondary electron (SE) and backscattered electron (BSE) mode (acceleration voltage of 30 KeV) after the samples were gold sputtered (Quorum Q150R ES plus sputter) so that electron conductivity was sufficient.

2.3 Biochemical methane potential assays

2.3.1 Inoculum and substrate

Inoculum was a liquid digestate from the same mesophilic biogas plant (Pustějov II-Zemspol Studénka Ltd) obtained the digestate for the production of BC. A centrifuge (BEHO CHC-61A) operating at 25°C and 1200 rpm was employed to generate a supernatant consisting of <3%wt. of solids that was used as the inoculum for the BMP tests. Prior to the tests, the inoculum was maintained at 4°C. Corn silage which obtained by the same agricultural biogas plant with inoculum and digestate was used as the substrate for all tests.

2.3.2 Anaerobic digestion tests

BMP assays conducted at mesophilic conditions (40±0.5°C) using 1 L glass bottle reactors with a working volume of 800 mL. The impact of each different BC was examined by adding 15 g of BC together with 15 g of substrate in a reactor. Each test was performed in duplicate to account for the measurements accuracy of material's heterogeneity and were accompanied by duplicate blank runs containing merely inoculum in the same quantity with the rest of reactors to determine the background gas produced by the inoculum. The real amount of methane generated in each reactor was calculated by subtracting the average amount of methane produced from the two blank runs. The incubation period was initially selected at 40 days assuming that the degradation process would be completed. However, within that period the daily biogas production did not drop below 1%vol. of the cumulative yields for all reactors, thus the incubation period was extended to 80 days (Salehiyoun et al., 2022). Prior to tests the reactors were purged with nitrogen and during the assays the reacting mixture was stirred at 100 rpm. Biogas volume and composition were monitored on a daily basis using graduated gas-collection burettes and a gas analyser (Geotechnical Instruments Biogas5000). The details on the set-up and procedure followed are available in Basinas et al. (2022).

2.4 Statistical analysis

Analyses and experiments were performed in duplicate and the presented results are the average values. Statistical analysis was used to identify any differences and similarities in biogas, CH_4, H_2, and H_2S generation in BMP tests using the two-sample t-test analysis of Microsoft Excel.

3. RESULTS AND DISCUSSION

3.1 Influence of chemical treatment on biochar properties

3.1.1 Effect on biochar compositional and pH characteristics

Proximate analysis results and the pH values for raw and pretreated BCs are shown in Table 1. Volatile content of sawdust (6.67%wt.) and digestate (7.96%wt.) BCs was relatively low but rational for chars produced at 800°C (Luz et al., 2018b). Volatile contents between 10.30 and 18.14%wt. that can be found in the literature for chars derived from biomass like straw, wood barks, stems, paddy straw etc. are probably related to a low temperature (500-600°C) applied for their production (Lee et al., 2013). Volatile matter increased 4.8- and 4.1-fold with the chemical oxidation of sawdust and digestate BC, respectively.

Concentration of fixed carbon (FC) in the sawdust char was at 92%wt. which was expected considering results for biomass BCs produced at lower temperatures (500°C) (Lee et al., 2013). Digestate char contained a much lower FC proportion (37.75%wt.). This was presumably attributed to the fact that the feedstock for the production of the digestate contained not only corn silage but also small proportions of other additives such as cattle slurry and manure that are known to possess a low FC concentration (Basinas et al., 2023). Oxidation had a strong effect on the FC of biomass BC reducing it by 27%, whilst a much smaller influence on the FC of digestate BC which reduced only by a 4%. As a consequence of the changes caused by the oxidation of biomass BC, FC in modified material was similar to that appeared for a waste-derived BC such as poultry litter (66.40%wt.), cocopeat (67.25%wt.) and hardwood (68.66%wt.), higher than that of BCs originated from similar materials such as straw (55.37%wt.) and switchgrass (54.60%wt), but lower than that of other biomass BCs like wood stem (83.47%wt.), palm kernel shell (PKS) (80.85%wt.), bagasse (80.97%wt.), safflower seeds (80.70%wt.) and fruit cuttings (79.85%wt.) (Kambo and Dutta, 2015; Lee et al.,2013; Luz et al., 2018b).

Ash content of sawdust BC (1.36%wt.) was low compared to the values appear in the literature for the specific material mostly ranging from 7.5%wt. to 21.7%wt. for BCs produced at temperatures between 650 and 700°C (Ghanim et al., 2020; Pariyar et al, 2020). However, similar low values (2.93%wt.) of ash in a sawdust BC have been recorded (Manyuchi et al., 2021). Digestate BC contained remarkably greater ash concentration (54.72%wt.), which was also far above the ash content of similar digestate-derived (17.50%wt.) (Zhou et al., 2017) and corn-derived chars (11.37%wt) (Liao et al., 2022). Ash concentration in the digestate BC was comparable to those (55.40%wt.) of biocarbons produced from OFMSW and temperatures up to 650°C (Wen et al., 2021). Ash content decreased 1.53- and 1.43-fold with HNO_3-modification for the biomass and digestate BC, respectively.

BCs were highly alkalic as indicated by their pH values (10.29 and 11.54 for sawdust and digestate BC, respectively). Elevated pH is typical for a high-temperature BC like the ones produced at 800°C mainly for two reasons. At first is a loss of acidic groups from BC structure due to polymerisation and condensation reactions taking place during heating (Gascó et al., 2005) and the second is an enhancement of ash proportion and accumulation of cations in material occurring at high pyrolysis temperature (Monlau et al., 2016). The oxidized samples converted from alkaline to acidic showing a drastic reduction of pH from 10.29 and 11.54 to 3.10 and 2.81 for biomass- and digestate-derived BC, respectively. A similar reduction of pH from 6.85 to 2.89 and from 8 to 4 was observed when a corn stover BC and a weed-derived char, both produced at 500°C, were treated with nitric acid (Gao et al., 2021; Güzel et al., 2017).

TABLE 1: Composition characteristics and pH of raw and modified BC. Standard deviations from two replicates are shown in parentheses.

Parameter	BCS	BCD	M-BCS	M-BCD
pH	10.29 (0.03)	11.54 (0.02)	3.10 (0.01)	2.81 (0.04)
V.M.[a] ($\%wt_{TS}$)	6.67 (0.19)	7.96 (0.26)	31.97 (0.33)	32.73 (0.69)
F.C.[b] ($\%wt_{TS}$)	92.00 (1.85)	37.35 (1.12)	67.39 (1.31)	35.97 (1.02)
Ash ($\%wt_{TS}$)	1.36 (0.11)	54.72 (1.09)	0.64 (0.04)	31.31 (0.55)
Elemental Composition ($\%wt_{TS}$)				
C	95.34 (1.25)	38.87 (1.02)	77.05 (0.66)	44.24 (1.07)
H	0.95 (0.01)	0.97 (0.02)	1.67 (0.03)	1.65 (0.03)
N	0.42 (0.02)	1.04 (0.04)	1.28 (0.01)	2.73 (0.05)
S	0.00 (0.00)	0.34 (0.02)	0.00 (0.00)	0.04 (0.00)
O[c]	1.94	4.06	19.36	20.03
O/C[d]	0.02	0.08	0.19	0.34
H/C[d]	0.12	0.30	0.26	0.45

[a] volatile matter, [b] fixed carbon, [c] by subtraction, [d] molar ratios

3.1.2 Elemental composition

Elemental analysis results for the raw and pre-treated BC are included in Table 1. Carbon content of BCS was particularly high (95.34%wt.) and similar to that of biomass BCs (89.30%wt.) produced at a temperature of 700°C (Chen et al., 2016) but generally greater that the carbon contained in biomass BCs produced at low temperatures (Luz et al., 2018a). Elevated carbon content mostly derives from a dehydration and depolymerization of plant biomass occurring with heating during pyrolysis that leads to a graphitization of carbon into organized layers (Ahmad et al., 2012; Chen et al., 2008). Carbon concentration in the digestate-derived char was substantially lower (38.87%wt.) and consistent with the values reported for agricultural digestate-derived BCs (37.28-45.30%wt.) (Tayibi et al., 2021; Wei et al., 2018). In general, elemental carbon content of BCs deriving from pyrolysis of agricultural digestates that can be found in the literature is highly variable (2.25-65.90%wt.), but particularly lower than that of biomass BCs (Catenacci et al., 2022). The carbon content of M-BCS was lower than that of BCS indicating that an amount of the element removed with the treatment with HNO_3. A carbon removal was not confirmed by the results for the digestate BC where the carbon content of M-BCD (44.24%wt.) was found not to be lower but 14% higher than that of BCD (38.87%wt.).

Nitrogen concentrations were equal or lower than the unit (1.04%wt. for BCD and 0.42%wt. for BCS) which is typical for digestate- and biomass-derived BCs, respectively (Basinas et al., 2023; Luz et al., 2018b). HNO_3 treatment caused a rise of 3-fold and 2.6-fold of the nitrogen concentration of digestates. This is not surprising since modification has been proved to advance the number of structures containing N-O bonds (nitro groups and nitrate complexes) (Fernando et al., 2021; Sajjadi et al., 2018). As for nitrogen, the measured oxygen for the two high-temperature BCs was significantly low at 1.94 and 4.06%wt. for BCS and BCD, respectively. Elemental oxygen increased with the acidic treatment, 9.98-fold and 4.93-fold in M-BCS and M-BCD, respectively (Table 1). Oxidation is one of the principal reactions taking place during treatment with HNO_3 provoking a substantial number of oxygenated acidic functional groups be introduced on carbon surface (Fernando et al., 2021; Güzel et al. 2017).

Amendments in molar oxygen to carbon (O/C) and hydrogen to carbon (H/C) ratio occurring with the acid treatment were considered in order to determine the influence of modification on the aromaticity index and polarity of BCs (Liu et al., 2020). In principle, a low O/C ratio indexes the hydrophobicity of a material whereas a low H/C ratio characterizes an aromatic material (Masebinu et al., 2019). For the two BCs, the O/C ratio was significantly small describing a hydrophobic nature for the materials. For the biomass BC, the H/C ratio was notably low showing that a high aromatization degree attained with pyrolysis at 800°C. For the digestate-derived BC, the ratio was found to be significantly higher (0.30) indicating a lower degree of aromaticity for the specific char. BCs showed enhancement of both molar O/C and H/C ratios with oxidation (Table 1). Oxidation with HNO_3 therefore allowed BCs to become less hydrophobic materials (Kobayashi and Kuramochi, 2022) with the modified digestate-derived BC displaying the greatest hydrophilicity (highest O/C ratio). Both BCs that sustained an HNO_3 treatment became also less aromatic with M-BCD exhibiting the lowest aromaticity (Shi et al., 2012).

3.1.3 Mineral composition

The main inorganic elements of raw and engineered BCs are shown in Table 2. Sawdust BC contained small amounts of minerals, mainly Ca and K, which is common for biocarbons originating from lignocellulose (Lee et al., 2013). P, Na and Si were also found in the biomass BC at proportions typical for biomass-derived chars (Lee et al., 2013; Pariyar et al., 2020). Digestate-derived BC was rich in all elements with Ca and K being the most abundant at the concentrations of 14.27 and 16.60%wt., respectively, which was in agreement with a similar digestate-derived BC produced at 600°C (Monlau et al., 2016). P, Si, Al, Mg and Na were also contained at higher concentrations than in the biomass char and at levels comparable to the results ap-

pear in the literature for similarly produced digestate chars (Basinas et al., 2023; Hung et al., 2017).

Inorganic content declined after treatment with nitric acid (Table 2). For M-BCS, the concentration of most substances approached a zero value with Ca being the most abundant at 0.38%wt. Reduction was also high for the digestate BC where modification resulted in a 70-75% decreased concentration of Ca, Al, K, and P and a complete disappearance of Mg. This was presumably ascribed to the fact that HNO_3 dissolves most inorganic substances. Nevertheless, a similar loss was not observed for Na and Si with modification of the digestate BC with HNO_3. In this case, M-BCD showed enrichment in Na and Si with Na concentration being increased 1.3-fold and Si proportion 1.9-fold (Table 2). Note that Si presence in biomass BC also remained unchanged at 0.03%wt. after treatment with HNO_3. It seems, therefore, that the Na and Si contained in digestate BC were strongly attached to the structure that despite the acid treatment they maintained and accumulated in the ash.

3.1.4 Surface morphology

BC materials are characterized by a developed porosity and high surface areas compared to the non-pyrolyzed material due to a thermal decomposition of organic matter and a release of volatiles which by being driven off the material create a network of pores in the organic structure (Monlau et al., 2016). The remaining solid is composed of highly concentrated aromatic carbon clusters forming a graphitic-like layered structure (Al-Wabel et al., 2013; Kambo and Dutta, 2015). The volatile release is more intense at high pyrolysis temperatures and therefore BCS and BCD, which produced at 800°C, were likely to show a highly-ordered porous structure. From Figures 1 (a) and (b), which show SEM images of the BCS and BCD, respectively it is seen that the surface area of both BCs contained pores at various shapes and sizes. A number of irregular folds were common on both surfaces although the two chars displayed significant differences in the other morphological characteristics. The surface of BCS was clearer than that of BCD allowing a number of thin pore walls and a uniformly distributed network of pores to be distinguished (Figure 1(a)). BCD also showed a well-developed porous structure, however, exhibited a rough surface that was characterized by a heterogeneous and pitted structure accompanied by an irregular pore arrangement (Hung et al., 2017).

The surface morphology of BCs appeared to differentiate with the acid treatment (Figure 1). Contrary to these results, Vu et al. (2017) found small differences between the surfaces of a corn-cob BC and its treated with HNO_3 counterpart. However, there are contrasting opinions about the effect of modification on the morphology of a BC. The surface of the raw biomass BC here, was smoother and more homogeneous than that of the M-BCS (Figures 1 (a) and (c)). A similar loss of smoothness and homogeneity was also observed by Li et al. (2019) for a raw and modified BC with manganese. The treatment of biomass char with HNO_3 led to a rougher and more cracked surface containing a great number of pores (Figure 1(c)). This was likely due to the activity of acid since early studies (Li et al., 2014) describe the occurrence of a partial collapse of pore walls with acid processing due to a removal of mineral matter and non-pyrolysed organics contained in BC.

In contrast to what was seen in biomass BC, the modified digestate BC presented a smoother surface than its untreated counterpart (Figure 1(d)). In this case, the bulges observed on the surface of the BCD were replaced by flatter and more compact formations of the surface of M-BCD. An extended network containing pores of all sizes was also visible. Cracking and fracture of micropores due to the introduction of oxygen functional groups in pore walls that were observed for acid-treated BCs (Cao et al., 2022; Li et al., 2014) could not be distinguished in the case of M-BCD.

3.2 AD of corn silage

3.2.1 Substrate properties

The characteristics of the corn silage and inoculum used in BMP tests are shown in Table 3. The pH value of corn silage (5.79) was close to those reported for the specific material (Tišma et al., 2018). However, the C/N ratio of 26 was rather low compared to the standards of corn biomass reported to be in the range of 32 to 45 (Şenol et al., 2020). In principle, a C/N ratio between 20 and 30, with an optimum at 25, is beneficial for AD (Panigrahi and Dubey, 2019). The C/N ratio of corn silage, therefore, implies that the material can attain a significant degree of degradability during AD.

3.2.2 Effect of biochar type on the AD of substrate

Figure 2 presents daily and cumulative biogas and biomethane generation results for the inoculum and corn silage. Daily yields present a peak early in AD indicating that the soluble organics contained in corn silage were likely consumed within the first 8-10 days of digestion. A total biogas amount of 0.526 $m^3kg_{VS}^{-1}$ was produced from the AD of the substrate, which was comparable with the average values reported for the mesophilic digestion of the specific feedstock (Tišma et al., 2018), but lower than

TABLE 2: Mineral composition of BCs before and after modification. Standard deviations from two replicates are shown in parentheses.

Sample	Element (%wt_{TS})							SUM
	Ca	Al	Mg	Na	K	P	Si	
BCS	0.68 (0.00)	0.00 (0.00)	0.00 (0.00)	0.06 (0.01)	0.30 (0.02)	0.07 (0.00)	0.03 (0.00)	1.14 (0.03)
BCD	14.27 (0.10)	1.39 (0.07)	1.60 (0.10)	1.02 (0.02)	16.60 (0.20)	4.15 (0.03)	7.00 (0.10)	46.03 (0.62)
M-BCS	0.38 (0.01)	0.00 (0.00)	0.00 (0.00)	0.02 (0.00)	0.02 (0.00)	0.07 (0.00)	0.03 (0.00)	0.52 (0.01)
M-BCD	3.78 (0.04)	0.35 (0.02)	0.00 (0.00)	1.36 (0.03)	4.94 (0.04)	1.10 (0.02)	13.48 (0.09)	25.01 (0.024)

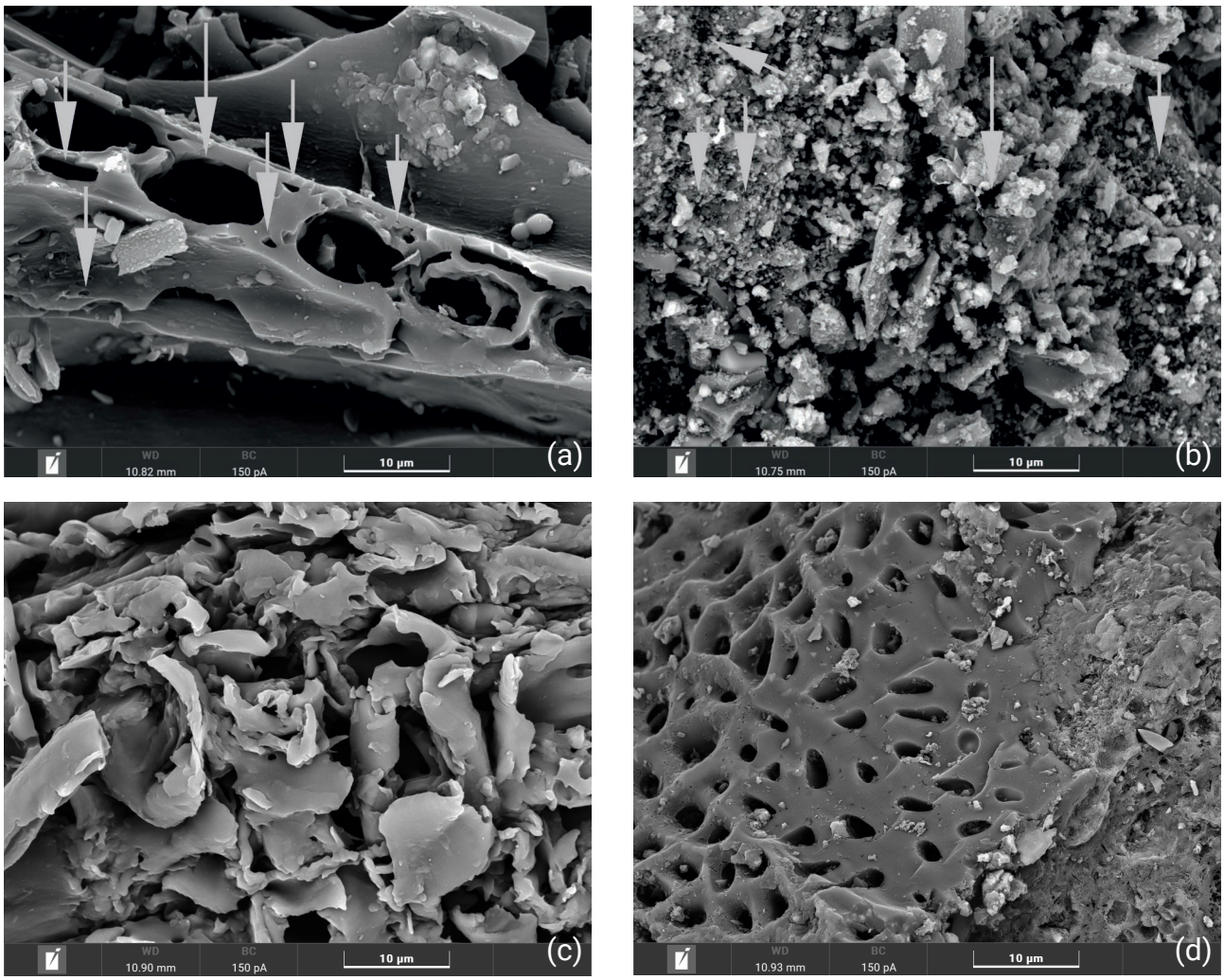

FIGURE 1: SEM images of (a) BCS, (b) BCD, (c) M-BCS and (d) M-BCD.

the biogas released from the AD of corn-derived materials (0.543-0.650 $m^3kg_{VS}^{-1}$) (Zieliński et al., 2019) and higher than that reported for other lignocelluloses such as wheat straw (0.432 $m^3kg_{VS}^{-1}$) (Yadav and Vivekanand, 2021). Total methane generation of 0.308 $m^3kg_{VS}^{-1}$ (Figure 2) was much higher than the total yields from a typical corn silage feedstock (0.153 $m^3kg_{VS}^{-1}$) (Xu et al., 2020) and also exceeded the production from other substrates like mechanically sorted-OFMSW (0.187 $m^3kg_{VS}^{-1}$), wheat (0.263 $m^3kg_{VS}^{-1}$) and rice straw (0.120 $m^3kg_{VS}^{-1}$) (Basinas et al., 2021; Mustafa et al., 2016). Lipid-rich substrates are characterized by enhanced AD performance. Besides, proteins have also positive effect on methane generation potential of a substrate (Xu et al., 2018). Corn silage contained a sufficient amount of proteins (4.26%wt_{TS}) (Table 3) that may explain the large methane production observed.

TABLE 3: Main characteristics of inoculum and substrate.

Parameter	Inoculum	Corn Silage
pH	7.97 (0.01)	5.79 (0.01)
TS (%wt.)	2.98 (0.03)	54.74 (0.14)
VS (%wt_{TS})	73.20 (0.18)	96.68 (0.21)
S (%wt_{TS})	0.49 (0.01)	0.32 (0.01)
C/N ratio	11.73	26.00
Proteins (%wt_{TS})	-	4.26 (0.16)
Carbohydrates (%wt_{TS})	-	0.30 (0.01)

TS=Total solids (105°C), VS=Loss on ignition (550°C)

To investigate the effect of BC on the AD of a lignocellulosic substrate, the biogas and methane generation potential of corn silage were determined in cultures with BCS and BCD addition. The results are shown in Figure 3. From the daily methane generation curves, a first production peak appeared on the third day of AD for all mixtures, which means that BC did not have any significant effect on the decomposition of easily degradable substances of corn. A shoulder existed at the last part of the peak extended from the fifth to twenty-fifth day. Within this period, corn silage showed a significant reduction in the daily methane yield especially on the fourth and fifth day. An extended production of VFA early in digestion and their accumulation might cause a system acidification and eventually a process inhibition. The systems containing BC showed a lower reduction in methane yields (Figure 3). BC due to its

high alkalinity can relieve an acid inhibition and concurrently enhance the efficiency of microorganisms to utilize organic acids in AD protecting a system operation (Pan et al., 2019). Methane generation was not abruptly reduced regardless of the type of BC used in the reactor. For the culture containing BCD a slight increase in methane yields was observed from the twenty-fifth to the thirty-second day which was represented by a small peak on the daily methane curve (Figure 3). This peak was not observed in the case of corn silage indicating that the BCD may provoke a degradation of complex substances, such as butyric acid (Ma et al., 2018).

From Figure 3 it is evident that both BC types had a positive influence on methane generation. In particular, cumulative methane production increased from 0.308 $m^3kg_{VS}^{-1}$ provided by the raw corn to 0.374 $m^3kg_{VS}^{-1}$ provided by the culture contained BCS corresponding to an increase of 1.21-fold. The methane generation attained by the culture with BCD addition was smaller (0.347 $m^3kg_{VS}^{-1}$) representing an increment of 1.13-fold (Figure 3). The growth was greater than that appeared in other studies where an increase of 1.10-fold (Luz et al., 2018a; Sunyoto et al., 2016) and 1.12-fold (Fagbohungbe et al., 2016) were reported with addition in the AD of lignocellulosic biomass of various types of BC materials prepared at temperatures between 450-550°C. The lower methane production from the culture with BCD addition was presumably a result of the fact that BCD contained a great proportion of ash, much higher than that of BCS (Tables 1 and 2), and thus its addition in the digester likely produced a cation toxicity effect, eventually having an adverse impact on methane generation (Linville et al., 2017).

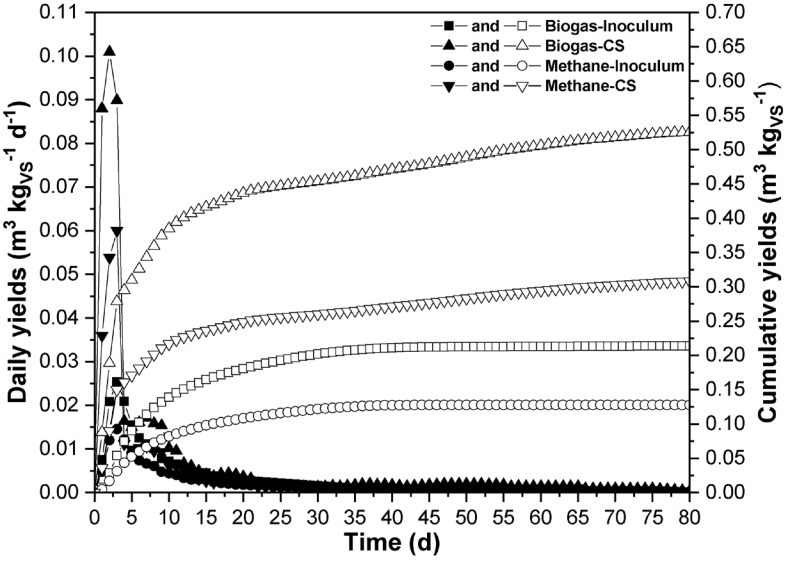

FIGURE 2: Daily (filled points) and cumulative (open points) biogas and methane production during AD of corn silage in BMP tests.

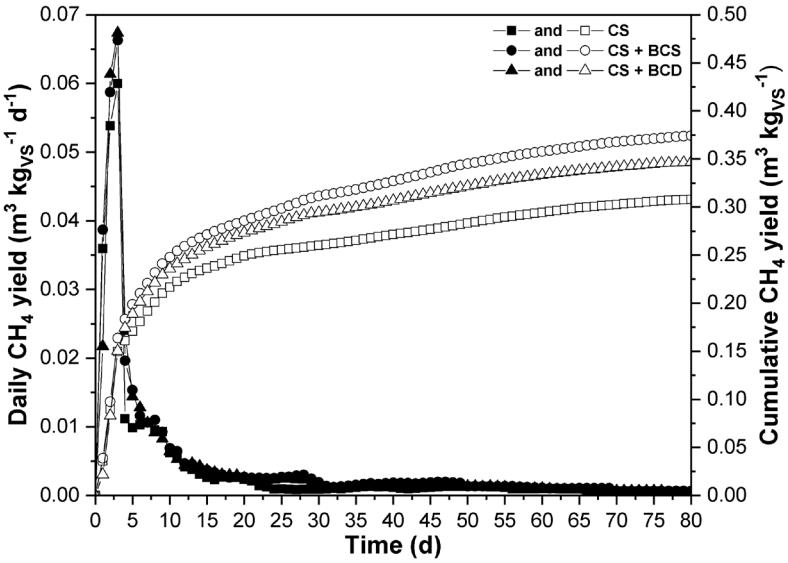

FIGURE 3: Effect of BCS and BCD on the daily (filled points) and cumulative (open points) biogas generation potential of corn silage under mesophilic AD conditions.

3.2.3 Biochar modification: Effect on the AD of corn silage

Oxidized BC can improve more than a non-pretreated BC the AD performance of a substrate (Gao et al., 2021). For this reason, BMP tests were conducted with addition of biomass-derived BC and digestate-derived BC that were previously modified with a nitric acid solution. Daily and cumulative methane generation results are shown in Figure 4. The cultures without and with M-BCS addition exhibited the highest methane generation on the third day of AD (0.060 and 0.045 $m^3kg_{VS}^{-1}d^{-1}$, respectively) whereas the culture with M-BCD on the fourth (Figure 4). Probably, M-BCD partially inhibited the operation of methanogens. Daily release curve shows that gas yields from the culture with M-BCD addition were significantly low for the first two days providing further proof that a potential inhibition might occurred early in process due to the M-BCD addition (Figure 4). Methane yields recovered on the third day whereas showed a peak (0.031 $m^3kg_{VS}^{-1}d^{-1}$) on the fourth day which was the maximum methane release rate attained by the specific culture. It should be emphasized here that the peak was lower by 93.6 and 45.2% than those attained by the cultures without and with M-BCS addition, respectively. It seems, therefore, that the addition of M-BCS and M-BCD led to a declined methane production rate.

A second peak that appeared for the AD of raw corn silage after the fifth day was shifted to the eighth and seventh day onwards for the cultures with M-BCS and M-BCD addition, respectively. The peak covered a period until the twenty-fifth day (Figure 4) within of which the reactor with M-BCD released the highest amount of methane followed by the reactor with M-BCS. The culture with M-BCD addition yielded daily a slightly higher amount of methane than the other two cultures during the next twenty-five days and a more significant amount of gas at around the fiftieth and sixty-fifth day of AD. This presumably means that BCD after its oxidation became more effective in promoting the conversion of persistent organic structures contained in corn silage (Kobayashi and Kuramochi, 2022).

Cumulative methane yields from the cultures with and without modified BC addition are included in Figure 4. Corn silage released gas with a high rate even by the first day. Cumulative methane production raised rapidly until the seventh day when the rate started decline and gas yields dropped below those of the culture with M-BCS addition. On the other hand, the culture with M-BCD presented significantly low yields at the initiation of AD and then a much low methane release rate. Nevertheless, the rate was stable enough that methane production became higher than that of the cultures without and with M-BCS addition after fifteen and twenty days, respectively. The two latter cultures consistently produced gas with a low and stable rate until the end of the BMP test. In contrast, methane production curve for M-BCD exhibited two points of maximum methane release rate (inflection points) during the 80 days of AD. This indicates the existence of two degradation regions which was also observed in earlier studies (Kobayashi and Kuramochi, 2022) and attributed to an effect of the BC on the degradation of easily and slowly degradable substrates. Hence, it seems that the M-BCD enabled decomposition of slowly digestible structures in corn silage (Ma et al., 2018).

Total volume of biogas and methane generated for the AD of corn silage with the addition of various types of raw and modified BCs are included in Figure 5. Methane release from the culture with M-BCS was 9% less than that from the culture with untreated BCS indicating that biomass-derived BC lost part of its capability to advance the methane generation when treated with HNO_3. Nevertheless, the two cultures (with untreated and oxidized biomass char) displayed the same total biogas generation (0.640 and 0.639 $m^3kg_{VS}^{-1}$, respectively). This finding suggest that the M-BCS impeded mainly the total meth-

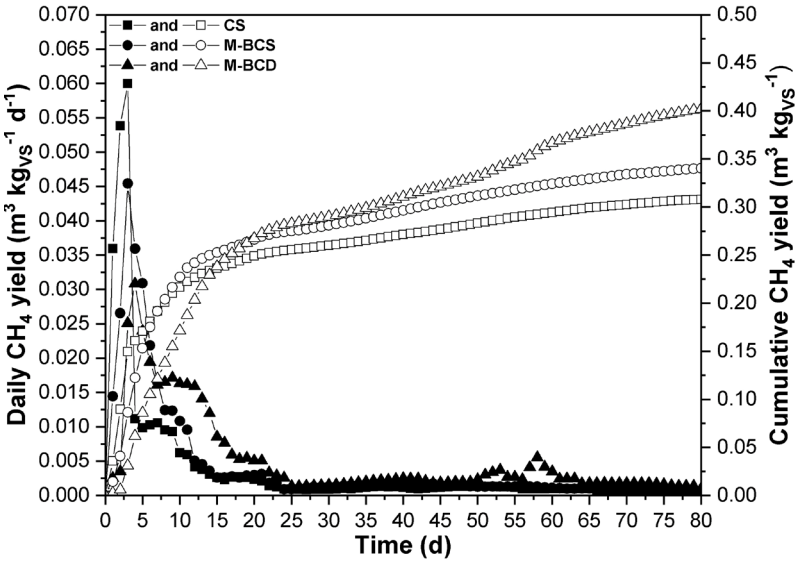

FIGURE 4: Effect of M-BCS and M-BCD on the daily (filled points) and cumulative (open points) methane generation potential of corn silage under mesophilic AD conditions.

anization of corn silage. The reason for the inhibition of methanogenesis could be likely related to the morphology characteristics of BC. As discussed above, biomass BC lost its homogeneity and smoothness of its surface with the treatment with HNO_3 obtaining a rougher and cracked morphology which may provided less support to microorganisms to develop.

Contrary to the BCS, modification of the BCD with HNO_3 led to an increased potential of the material to catalyse the AD process as indicated by the augmented total methane production attained by the culture with M-BCD addition compared to the culture with untreated BCD (Figure 5). The fact that the surface was smoothened, flattered and contained a well-developed network of pores (Figure 1) shows that BC morphology was presumably reason for the performance of the modified BC in an AD system. In addition, the cation toxicity effect of BCD on AD observed due to high proportion of minerals is also expected to be diminished due to the removal of a major part of the ash and minerals by the material with the HNO_3 oxidation (Tables 2 and 3).

Biogas and methane generation attained from the reactor with BC addition could potentially be influenced not only by the properties of BC but also by the generation of H_2S which is known to have an inhibitory effect on AD (Romero-Güiza et al., 2014). H_2S obstructs the process in two ways: competence of sulphate reducing bacteria and methanogens for the consumption of organic substances and a toxic effect that H_2S exerts on methanogenic bacteria by diffusing through their cell membrane into their cytoplasm (Chen et al., 2008). Figure 6 provides results for H_2S evolution over the 80 days of digestion. H_2S yields from most of the cultures with BC remained steadily below those from the culture without BC for the entire digestion period. This suggests that BC was capable to capture H_2S mitigating its effect on the AD, which likely explains an increment of methane and biogas yields from the reactors containing BC (Choudhury and Lansing, 2020).

As seen from Figure 6, H_2S release from the reactors with BCD and M-BCD addition did not follow the same behaviour and especially in the former case H_2S production appeared to be much greater than that from the reactor without BC addition. In particular, for the reactor containing BCD, H_2S yields abruptly increased at extremely high level (>2100 ppmv) even by the first day of digestion, remained at that level for about eight days before being dropped to around 1000 ppmv and then progressively to 300 ppmv until the end of the 80 days of digestion. Parkin et al. (1990) reported significantly hindered biogas release at H_2S concentrations higher than 100ppmv, which might explain the low methane generation observed for the culture with BCD addition. Methane release from the specific culture was higher than that from the reactor without BC and lower than that appeared for the culture with BCS addition. It can be assumed, therefore, that the advantage of an improved methane generation derived by the implementation of BC in the system was at least partially compensated by an inhibition originated from H_2S.

Figure 6 indicates that the culture with M-BCD also displayed a significant H_2S release, however, in this case the yields were at 2050 ppmv only for the initial day of digestion. The abrupt increase of H_2S during the first day coincided with a failure of the system to produce methane (Figure 3). From the second day, H_2S release fell-off to values lower than 100 ppmv where kept until the end of the BMP assay. It is interesting to note that H_2S release from the culture with M-BCD addition was permanently lower than those attained from the other cultures and concurrently the specific culture exhibited higher methane yields. Given that for all the other bioreactors, concentration of H_2S was over 100 ppmv it can be hypothesized that an inhibition in methane generation existed in all cases. It appears, therefore, that the greater methane release from the culture with M-BCD

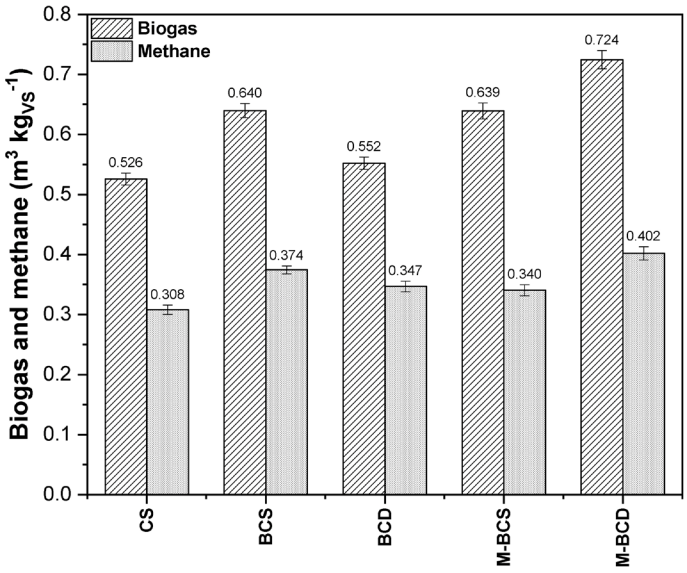

FIGURE 5: Biogas and methane generation potential of corn silage for the cultures without and with BC and modified BC. Mean values±standard deviations from two replicates are shown.

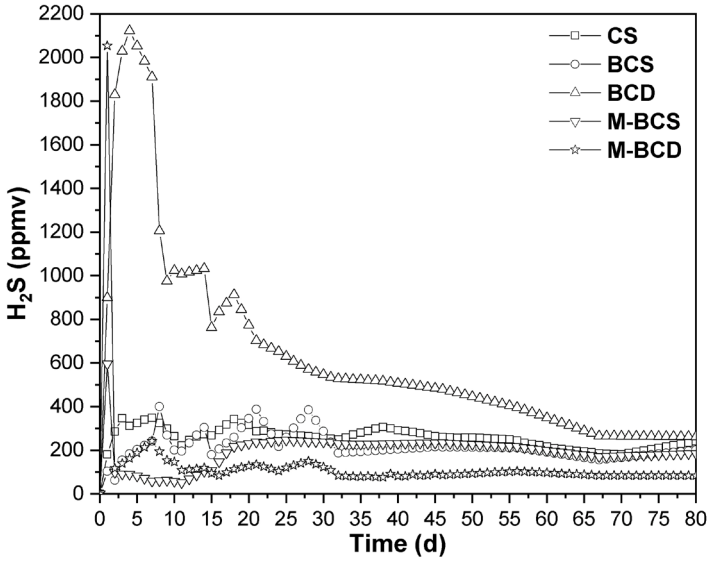

FIGURE 6: Daily hydrogen sulfide release during AD of corn silage incubated with and without BC.

addition compared to the rest of the reactors might be related to a capability of the specific BC to alleviate any inhibition induced by H_2S.

4. CONCLUSIONS

A typical biomass- and a digestate-derived BC were subjected to chemical modification with nitric acid and used as additives in the digestion of corn silage to determine the influence of oxidation on the capability of the different types of BC to improve the efficiency of the AD of biomass.

Both biomass and digestate BC had a positive effect on methane generation from the AD of corn silage. BCD addition improved methane yields from 0.308 $m^3kg_{VS}^{-1}$ released from the culture without BC to 0.347 $m^3kg_{VS}^{-1}$, whilst BCS was more efficient resulting in a total gas release of 0.374 $m^3kg_{VS}^{-1}$. Chemical modification reduced the pH of BCS from 10.29 to 3.10 and that of BCD from 11.54 to 2.8 converting BCs from alkalic to acidic, while concurrently differentiated their surface morphology. For M-BCS ash proportion was minimal at 0.64%wt_{TS} and mineral concentrations were almost nullified (<0.38%wt_{TS}), whereas for M-BCD modification reduced the ash fraction from 54.72 in BCD to 31.31%wt_{TS} in M-BCD and the concentration of each of the Ca, Al, K and P by 70-75%. The culture with M-BCS provided 9% less methane than the culture with the untreated BC, thus the chemical treatment had a slight negative impact on the catalytic activity of biomass char. In contrast, the culture with modified digestate char released the highest amount of gas (0.402 $m^3kg_{VS}^{-1}$) than all cultures. This ascertained to be a result of an increased capability of the material to assist conversion of persistent and slowly digestible organic structures contained in corn silage and to retain the H_2S yields at a level lower than 100 ppm. Therefore, M-BCD presented a higher potential to improve the efficiency of an AD system than the biomass BC (untreated and modified) and this capability could be further improved with a potential enhancement of the H_2S uptake particularly at the initiation of AD process.

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THERMOCHEMICAL VALORISATION OF WASTE: PYROLYTIC CONVERSION OF HORSE STABLE RESIDUE INTO BIOCHAR

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ABSTRACT

In this study, horse stable waste (horse manure, peat and wood sawdust) was processed under pyrolytic conditions. The chemical and physical properties of biochar obtained from different mixtures of horse stable residues were compared. All measurements followed an experimental design using a mixture model. This approach allowed the properties of any combination of ingredients to be predicted and the influence of each component on the final value to be estimated, with very good agreement between predicted and observed values. The results of the analysis of pH, polycyclic aromatic hydrocarbons (PAH), specific surface area (SSA) and CHNSO (carbon, hydrogen, nitrogen, sulphur and oxygen) showed that all possible combinations of materials can be used as soil amendments, since: an alkaline pH (>7) prevents soil acidification and a concentration of PAH below the limit (ΣPAH<12mg/kg) does not pose a risk to human health. A high SSA value (>180 m^2/g) and a different particle size distribution (PSD) provide habitat for microorganisms, increase water retention capacity and reduce greenhouse gas (GHG) emissions from the soil.

1. INTRODUCTION

Livestock waste is a valuable and important resource. Animal manure is commonly used in agriculture as an organic soil improver due to its high nutrient content (phosphorus, nitrogen and potassium). However, this type of residue has some serious drawbacks: manure leaks during storage and disposal can negatively impact soil and water quality and cause environmental problems (US Environmental Protection Agency, 2017). Its decomposition, when stored or managed in lagoons or storage tanks, produces enormous amounts of greenhouse gases. Uncomposted horse manure has been shown to immobilise nitrogen in the soil, affecting crop growth. In addition, the use of horse manure as a soil amendment poses the problem of weed seeds that can germinate after composting. It is estimated that 700 000-800 000 m^3 of this material is produced annually in Finland (Nikama et al., 2015), most of which is incinerated as waste, leading to significant CO_2 emission problems.

Horse bedding in Finland generally consists of a mixture of wood and peat, which provides a good balance between manure adsorption and animal well-being.

Peat consists of partially decomposed organic material, where decomposition by plants or animals is inhibited by acidic and anaerobic conditions (Syifa Rinaldi et al., 2019). In contrast to other countries and organisations, Finland classifies peat as a "slowly renewable biomass fuel" and allows its combustion for heat and electricity production (Finnish Ministry of Trade and Industry (KTM), 2000). The consequences of this process mainly concern CO_2 emissions, as its combustion produces 106 gCO2/MJ (more than coal), and the extraction of peat from peatlands negates its natural carbon sink effect. In fact, peat naturally binds and stores the carbon dioxide produced during its formation (Hagberg et al., 2008). Wood is one of Finland's most important natural resources and has wide range of industrial applications, from the sawmills to pulp and paper. Of greater interest is its combustion with manure and peat. Wood is often added to manure and peat fuels to improve the LHV and reduce carbon dioxide emissions (Hagberg et al., 2008). In general, there are more valuable options for valorisation of these residues than pure incineration. These include anaerobic digestion and gasification, which produce biogas that can be used directly for heating and electricity generation. Another option would be to use these materials as a feedstock to produce biochar through a slow pyrolysis treatment. This innovative technology is very promising due to its social, economic and environmental benefits: low operating costs at small and large scales (atmospheric pressure conditions and moderate temperatures),

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sustainable waste management and useful applications of the product (Adánez-Rubio et al. 2021), (Li et al. 2021). Biochar is defined as a solid material produced by the thermochemical conversion of biomass in an oxygen-free or low-oxygen environment; in principle, the carbon sequestered in biochar by pyrolysis must remain in this form for a long time (land use). In contrast, the use of charcoal as a fuel or carbon source for chemicals involves CO_2 emissions (Schmidt et al., 2021). Biochar has great potential to sequester greenhouse gases and could play an important role in waste management in the near future. This potential can be summarised in the following points:

- Long-term sequestration of Carbon due to its stability;
- Cogeneration of primary energy during the pyrolysis process. Use of this primary energy in industry, thereby reducing emissions;
- Reduction of nitrous oxide and methane emissions resulting from biomass decomposition;
- Reducing the use of landfills, thereby reducing greenhouse gas emissions;
- Improvement of areas arable lands;
- Reducing the energy used to transport waste over long distances;

  (Gunarathne et al., 2019), (Li et al. 2021), (Liu et al., 2014), (Schmidt et al., 2021).

The aim of this paper is to provide indicators for better use of agricultural and industrial residues through the use of a thermochemical conversion process.

In summary, the first part of this paper is dedicated to the physical and chemical characterisation of biochar products obtained by slow pyrolysis treatment of horse stable wastes (horse manure, peat and wood sawdust). In the second part, a Mixture model for residues (which are inseparably bounded after pyrolysis) is established to predict the reaction for each empirically producible combination of components and to estimate the influence of each component in combination with the others. The Mixture model is a powerful tool for combining several data-generating processes into a single model. Finally, the quality of the biochar and its potential use as a soil amendment are assessed, considering the soil protection thresholds set by European legislation.

2. MATERIALS AND METHODS

2.1 Biochar production

2.1.1 Horse stable residues

In this study, stable waste consisting of horse manure, peat and wood sawdust, was used to produce biochar. All these wastes were collected directly from the Espoo Riding School near Helsinki. The peat used is a commercial peat produced in Estonia called "BALTIC PEAT" with an organic matter content of at least 90%, a pH of 3,5-4,5 and a degree of humidification of H2-H6 (all data are taken from the product label). The wood sawdust is a commercial product called "POLKKYpets" produced by the company "Poelkky Oy" (Finland) from Finnish pine and spruce sawdust.

2.1.2 Samples preparation

It was found that the moisture content of manure and peat as delivered is much higher than that of sawdust, almost 53% for peat and as much as 68% for manure. Since the aim of this work is to characterise a mixture of these three elements, it can be assumed that this mixture is subjected to an industrial-scale drying process before pyrolysis. Therefore, to make all values comparable, the initial moisture content of peat and manure was reduced by drying. Specifically, freshly collected horse manure was stored at room temperature with forced ventilation for seven days, while peat was dried in a ventilated oven at 40°C for almost 18 hours. Wood chips MC: 7,6%, manure MC: 7,1%, peat MC: 8,8%. All the original biomass was ground (2-5 mm). This procedure allowed the homogenisation of both pure materials, as peat consists of different elements, and mixed materials. Seven diverse types of samples were prepared and characterised. Table 1 shows the composition of each sample, and all productions were conducted in triplicate for statistical reasons.

2.1.3 Experimental setup

Pyrolysis of all samples was performed in a quartz tube furnace (NBD-O1200, Nobody Material Science and Technology CO., LTD, China). The experimental setup and photographs are shown in Figure 1. Oxygen-free conditions were achieved by a nitrogen flow of 10 mL/min controlled by a flowmeter, and nearly 2 g of samples per crucible were processed. In their previous work (Caro et al., 2021), Caro et al. found optimal values for the process parameters for manure, namely a heating rate of 10°C/min, a HHT (highest heating temperature) of 600°C and a residence time of 2 h. These values were also taken as the minimum optimal values for this work, as the focus of the study is on the mixing of the three materials. The synthesis gases produced during pyrolysis were condensed using a water cooling system. The operating scheme of the furnace is shown in Figure 1(C).

2.2 Biochar characterisation

2.2.1 TGA analysis

Thermogravimetric analysis (TGA) was carried out on both the original biomass and the biochar samples obtained. A TGA Q500 TA instrument (USA) was used for this

TABLE 1: List of all the samples used to produce biochar, with each specific original biomass composition.

Sample	Horsemanure	Peat	Wood
	[%]	[%]	[%]
Manure	100	0	0
Peat	0	100	0
Wood	0	0	100
MPW (manure-Peat-Wood)	33,33	33,33	33,33
MP (Manure-peat)	50	50	0
MW (Manure-wood)	50	0	50
PW (peat-wood)	0	50	50

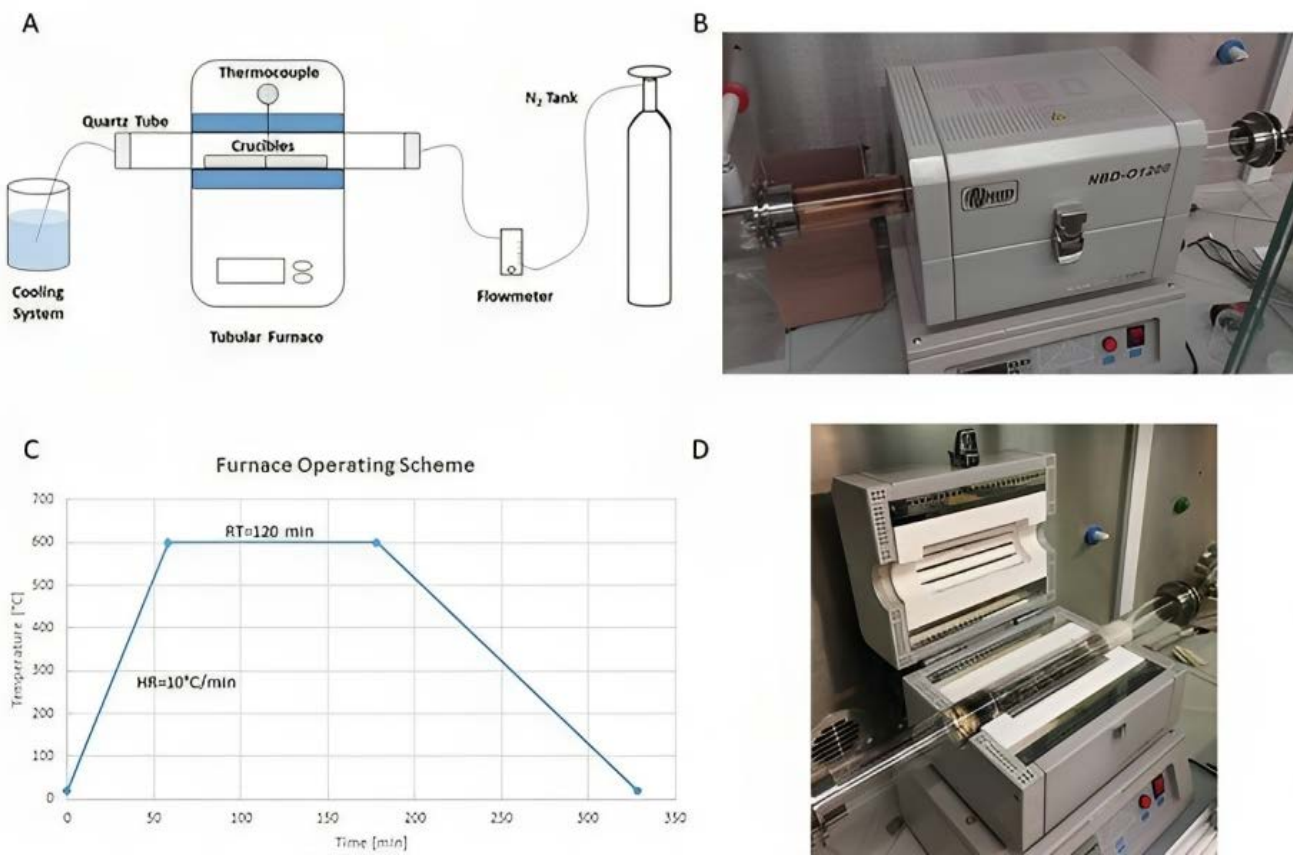


FIGURE 1: Experimental setup scheme (A), furnace operating scheme (C), closed furnace picture (B) and open furnace picture (D).

analysis. The test method used consisted of heating the sample in an inert environment (provided by a nitrogen flow of 60 NmL/min) from 20°C to 900°C at a heating rate of 10°C/min and a final isothermal combustion at 900°C with pure oxygen for 5 minutes.

2.2.2 Proximate analysis

Proximate analyses were performed on both the original biomass and the biochar produced. As for the biomass, all analyses were performed according to the ASTM standard. For moisture content (MC), ASTM E1756-08 was followed (ASTM, Standard Test Method for Determination of Total Solids in Biomass, 2006). Ash content was determined according to ASTM E1755-01 (ASTM, Standard Test Method for Ash in Biomass, 2015). The volatile matter (VM) content was determined according to ASTM E872-82 (ASTM, Standard Test Method for Volatile Matter in the Analysis of Particulate Wood Fuels, 2013). Finally, the fixed carbon (FC) content was determined as the difference between 100 and the sum of the other contents. On the other hand, the proximate analysis for biochar samples was performed according to the EBC (European Biochar Certificate) analysis methods (Schmidt et al., 2021). These methods are similar to the previous ones, with only minor differences in the target temperatures. 2.2.3 CHNSO analysis

The carbon, hydrogen, nitrogen, sulphur and oxygen contents of the biochar were determined using a Perkin Elmer CHNS/O 2400 series analyser II (dry combustion method). In particular, the C, H, N and S contents were measured directly with the instrument, while O was calculated as the difference between 100 and the sum of the other contents and ash according to the EBC guideline (Schmidt et al., 2021), as the sample is assumed to consist essentially of these elements. For statistical reasons, this analysis was performed for the mixture model in triplicate for the MPW mixture, in duplicate for the pure materials (M, P, W) and in single for the MP, MW and PW mixtures (see section 4).

2.2.3 SSA Analysis

Specific surface area (SSA), pore volume and pore size of all biochar produced were determined by Bruner-Emmett-Teller analysis (using Tristar II -Micrometrics, USA, with covered liquid nitrogen tank). The Barrett-Joyner-Halenda (BJH) method was used to estimate pore size distribution based on pore volume. Micropore volume and surface area were determined using the T-plot method These results were compared with the total pore volume and SSA determined using the Brunauer-Emmett-Teller (BET) equation. The contribution of micropores and meso-macropores was expressed as a percentage. All methods used are in accordance with standard procedures for porous materials (Phuong et al., 2016).

2.2.4 PAH Analysis

PAH analysis was performed on the same number of samples as for CHNSO analysis. The sample (approximately 0,5 g dry weight) was weighed into an extraction thimble

and extracted with 50 mL of analytical grade toluene for two hours (reflux method). Finally, the extract was concentrated to 10 mL by evaporation under reduced pressure. The PAHs in the extract were analysed using a gas chromatograph and mass spectrometer (Agilent GC 7890A and 5975C Inert MSD). An internal standard was used to quantify the PAH concentrations. The column was an HP 5MS (30 m x 0,25 mm x 0,25 µm). The temperature programme was as follows 90°C (0,5 min), 20°C /min to 250°C; 5°C / min to 275°C; 20°C /min to 320°C (5 min). The temperatures applied were as follows: Transfer line: 280°C; MSD: 150°C; injector: 250°C. The injection volume was 1,0 µL and the carrier gas flow (helium) was 1,5 mL/min (International Organisation for Standardisation 18287:2006, 2006).

2.2.5 pH Analysis

The pH of all samples, both the original biomass and the produced biochar, was determined using the same procedure proposed in the EBC analytical methods (Schmidt et al., 2021). A 25 mL volume of 0,01 M $CaCl_2$ solution was prepared and added to a 5 mL volume of the sample in a glass vessel. The solution was stirred for 1 hour to obtain a homogeneous suspension. After this treatment, the pH was measured using an Orion 2 Star pH meter (Thermofisher Scientific, USA).

3. RESULTS AND DISCUSSION

3.1 Feedstock physical and chemical properties

In Table 2 the physical and chemical properties of the raw materials are shown.

In terms of volatile content, the highest value is attributed to wood with 87,4%, followed by manure and peat (77,2% and 74,8% respectively). As shown in Table 2, the ash content of the biomass varies considerably depending on the species. As expected, the ash content of wood is almost zero, while the ash content of manure is the highest (7,4%), which is due to the high mineral content. The content of fixed carbon ranges from 12,3% to 23,8%. All the data obtained are in good agreement with the TGA results (Figure 2 and Figure 3).

3.2 TGA Analysis results

As reported by (Hernandez-Mena et al., 2014) and (Katesa et al., 2013) in their analyses, cellulose, hemicellulose and lignin behave quite differently under thermal decomposition. According to (Hernandez-Mena et al., 2014), the degradation temperature of cellulose and hemicellulose is 200-360°C and 360-600°C for lignin; (Katesa et al., 2013) report a range of 250-350°C for cellulose and hemicellulose and 350-750°C for lignin.

In Figure 2, the TGA curves for all materials show the highest mass loss up to 350°C, about 55% for manure and peat and even more for wood. These results agree well with the structural composition of these materials where, for example, the sum of cellulose and hemicellulose is almost 58% for manure (Caro et al., 2021) and on average 65-75% for wood (Pettersen, 1984). Furthermore, the graph shows that a constant mass is only reached at a temperature of 550°C, i.e. complete lignin degradation. Since higher lignin content leads to higher biochar yields as described in (Lehmann et al., 2009), peat and manure are expected to give the highest yields, followed by wood. Considering the data from the TGA curves in Figure 2, a first mass loss in a temperature range between 30-150°C is due to water evaporation, which is consistent with the literature from (Hernandez-Mena et al., 2014) and (Katesa et al., 2013). The second and largest, which occurs in the 200-550°C range, is mainly related to the release of volatiles (CO_2 and CH_4). Finally, from 600°C to 900°C, the last mass loss reflects the content of fixed carbon and ash (García et al., 2013). As can be easily seen, the amount of VM produced from biomass is directly related to the content of cellulose and hemicellulose (partly also lignin), while the fixed carbon is mainly due to lignin. The TGA of wood has the highest slope, followed by manure and peat, so a higher value of volatiles is expected in this material. On the other hand, peat and manure show higher weight losses at 900°C (about 30%). Wood shows a mass loss of almost 20% at 600°C, which increases to 10 and 15% for manure and peat respectively. As a result, the biochar yield is expected to be higher from peat, followed by manure and wood.

Figure 3 shows that all curves follow a similar trend of thermal degradation trend up to 500°C. After that, there is a clear difference between the curves, resulting in a higher mass loss for wood biochar (almost 25% in the range 500-900°C) compared to peat and manure. In particular, peat biochar shows the lowest total weight loss, less than 10%; this is closely related to the original mineral content of the feedstock.

3.3 Physical and chemical properties of the raw materials and their biochar

Table 3 provides an overview of the physical and chemical properties of the biochar. As expected, the yields vary depending on the feedstock. In particular, it is again shown that biochar produced from manure has higher values than that obtained from agricultural residues. In fact, the yield of wood is 21% higher, while that of horse manure is 10% higher.

Regarding the properties of the biochar, the volatile matter content decreases significantly, while the ash and

TABLE 2: Results of physical and chemical properties of raw materials.

Material	Sample	Ash	VM	FC	C	H	N	S	O	H/C	O/C	pH
		[%db]	[%db]	[%db]	[%]	[%]	[%]	[%]	[%]	-	-	-
Biomass	Manure	7,4	77,2	15,4	47,3	6,1	1,7	0,8	36,1	0,13	0,76	6,9
	Wood	0,2	87,4	12,3	50,0	6,0	1,0	1,0	42,0	0,12	0,84	4,3
	Peat	1,4	74,8	23,8	56,0	5,0	1,0	1,0	37,0	0,09	0,66	3,1

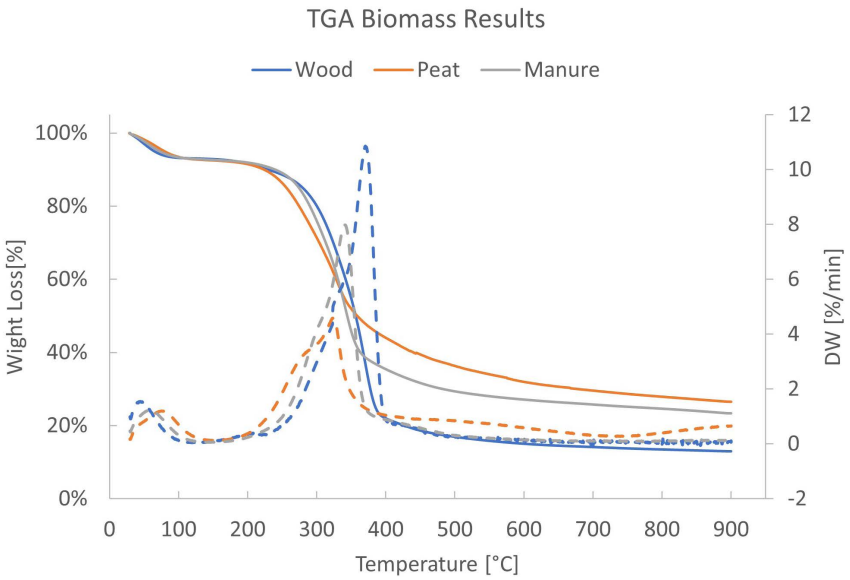


FIGURE 2: TGA (solid line) and DTG (dash line) curves of the three different biomass.

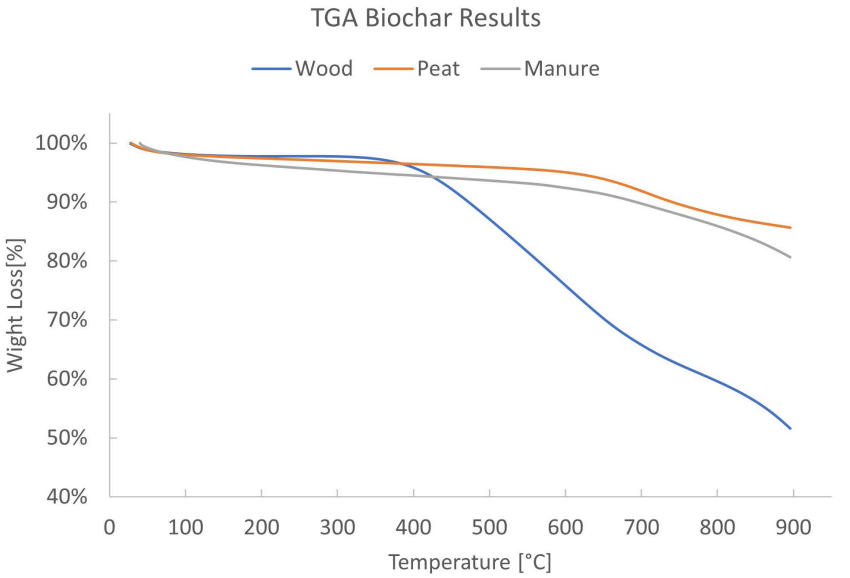


FIGURE 3: TGA of wood, peat and manure biochar.

fixed carbon content show an opposite trend. As with the original biomass, manure biochar has the highest ash content at almost 22%, while wood has the highest VM value. The carbon content varies between 68% (manure) and 90% (peat and wood). The carbon content increases significantly, by almost 30%, when the biomass is pyrolysed. This increase is accompanied by a decrease in the H and O content, a phenomenon well confirmed in the literature by the works of (Jindo et al., 2014), (Bayan, 2012) and (Lee et al., 2013). On the other hand, the correlation between nitrogen in the initial biomass and its variation during pyrolysis is not well understood, in this case showing different tendencies depending on the feedstock. As for the sulphur content, its proportion in horse manure decreases after pyrolysis, which is common for manure-based biochar, where it is more sensitive to mass loss in the vapour phase. It is suggested that part of the sulphur contained in the volatile organic compounds is lost at 350°C and the remaining is more resistant to bond breakage in accordance with the work of (Cantrell et al., 2012). Mixtures of pure elements show an average value weighted by mass composition. The reduction of these two ratios after pyrolysis is the result of dehydration and decarboxylation reactions (Jindo et al., 2014). In general, a low O/C ratio corresponds to low polarity and a hydrophilic surface, while the higher the degree of aromatisation and charring, the lower the H/C ratio, resulting in extremely stable structure formation (Gai et al., 2014). Peat and wood biochar (0,08) show better stability than manure (0,31), especially their location in the low H/C - higher O/C range can be attributed to the fact that ash

TABLE 3: Results of physical and chemical properties of biochar.

Material	Sample	Ash	VM	FC	C	H	N	S	O	H/C	O/C	Yield	SSA	PV	PS	pH
		[%db]	[%db]	[%db]	[%]	[%]	[%]	[%]	[%]	-	-	[%]	[m²/g]	[cm³/g]	[nm]	-
Biochar	Manure	21,8	6,1	72,1	68,2	1,7	2	0,2	20,9	0,02	0,31	29,0 ± 0,002	45 ± 6,9	0,03 ± 0,003	2,9 ± 0,14	10,1 ± 0,02
	Wood	1,4	22,3	76,3	89,8	2,1	0,6	0,2	6,9	0,02	0,08	19,4 ± 0,009	351,3 ± 5,17	0,19 ± 0,006	2,2 ± 0,09	7,6 ±0,04
	Peat	3,1	4,1	92,8	87,3	2,5	1,7	0,4	6,7	0,03	0,08	27,6± 0,04	307,1 ± 10,85	0,18 ± 0,001	2,3 ± 0,08	7,4 ± 0,03
	MPW	16,3 ± 0,2	-	-	80,1 ± 0,02	2,1 ± 0,00076	1,7 ± 0,001	0,2 ± 0,001	12,9 ± 0,02	0,03 ± 0,005	0,16 ± 0,03	27± 0,014	227,8 ± 4,15	0,13 ± 0,003	2,2 ± 0,02	8,8 ± 0,01
	MP	13,1	-	-	74,4	2,1	1,5	0,2	17,3	0,03	0,23	30,6± 0,002	197,2 ± 4,43	0,11 ± 0,001	2,3 ± 0,08	9,2 ± 0,03
	MW	13,6	-	-	78,3	2,2	1,4	0,2	14,2	0,03	0,18	25,6± 0,001	180,8 ± 15,37	0,1 ± 0,008	2,2 ± 0,02	9,3 ± 0,02
	PW	2,9	-	-	78,6	2,2	1,2	0,2	16,9	0,03	0,21	26,5 ± 0,005	313,5 ± 8,85	0,17 ± 0,0016	2,2 ± 0,04	7,5 ± 0,06

minerals change their composition by melting and sintering during pyrolysis, as shown in (Xin et al., 2014). As far as the BET analysis is concerned, the average SSA value for all the biochars studied varies between 45-350 m^2/g. This value was measured according to the multipoint surface model for materials with large variations in pore size. Considering that biochar has a complex structure in which all types of pores coexist, this measurement should be representative, as the single-point measurement at p/ps = 0,299, which has higher values in all analyses performed, overestimates this value (Bachmann et al., 2016). As expected, wood biochar has the highest SSA value and manure the lowest. These results are in good agreement with the literature (Caro et al., 2021), (Singh et al., 2010) and (Cantrell et al., 2012). The biochar produced from the mixed materials has high SSA values of over 150 m2/g.

Figure 4 shows how the PSD value varies depending on the feedstock. In particular, manure biochar has the highest proportion of macropores at almost 20%, while peat and wood have a higher proportion of micropores. The high proportion of micropores is also reflected in the proportion of total area and volume (Figure 5-6). The figures for the PSD and area fractions are in good agreement with previous studies, while the volume fractions show a higher proportion of micropores (Phuong et al., 2016). Furthermore, (Ioannidou et al., 2007) found that lignin develops macropores while cellulose favours the formation of micropores, which is in perfect agreement with the results obtained.

3.4 AH (polycyclic aromatic hydrocarbons) Analysis results

In Table 4, total PAH concentrations range from 4 to 9,1 mg/kg. All determined values are well below the EBC limit of 12 mg/kg, so that all biochar can be applied to the soil (Schmidt et al., 2021). Biochar mixtures do not behave as a mass-weighted value. In fact, PAH levels are higher than expected in all the mixtures studied, especially when peat is present. The explanation for this phenomenon is not fully understood and needs further investigation. A possible correlation between the SSA of biochar and the pore size distribution and/or the functional surface group with the PAH concentrations could provide an explanation. In general, all these values are expected to be higher than those

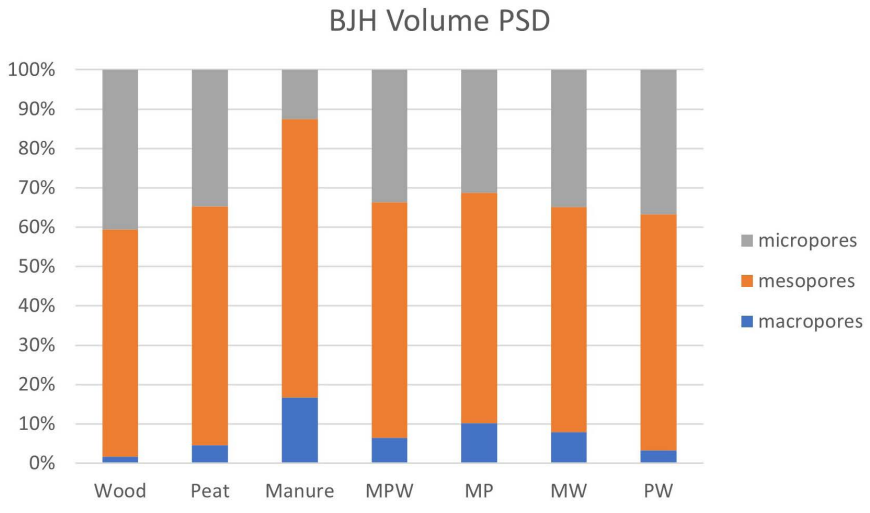


FIGURE 4: Particle size distribution of all studied biochar derived using BJH model for pore volume.

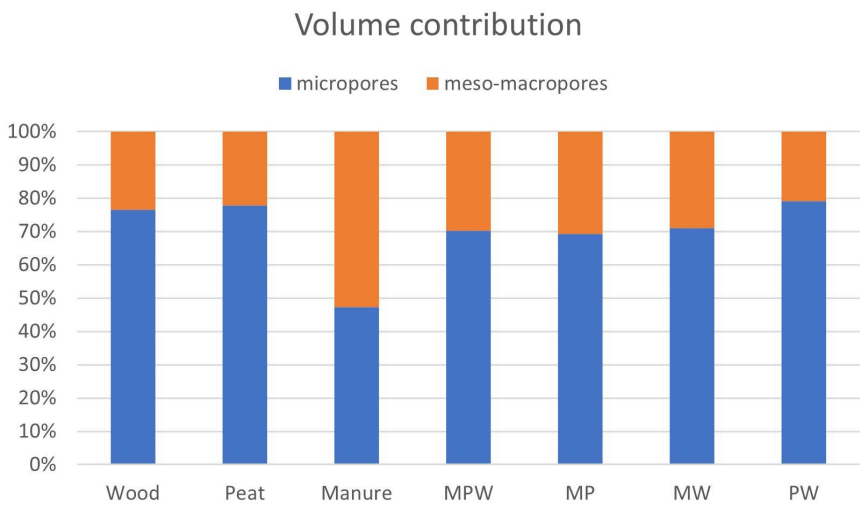


FIGURE 5: Contribution of micro, meso and macropores volume in the total pore volume for all studied biochars according to BET and t-plot data.

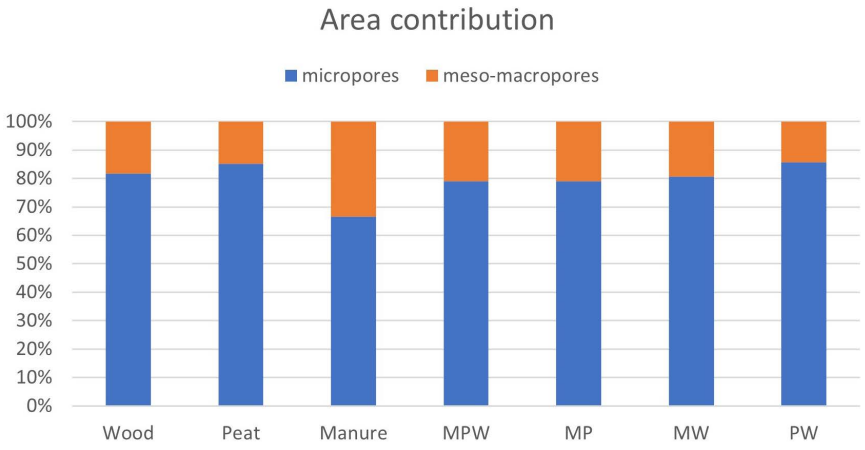


FIGURE 6: Contribution of micro-, meso- and macrospores volume in the total pore area in total SSA for all studied biochars according to BET and t-plot data.

obtained from the analysis of the same biochar produced on an industrial scale. This is due to the small size of the quartz tube, which does not allow perfect evaporation of the gaseous PAHs deposited on the biochar after condensation. Furthermore, Table 4 shows that naphthalene is the most abundant compound; this result is in good agreement with the literature (Bachmann et al., 2016).

4. EXPERIMENTAL DESIGN USING MIXTURE MODEL

4.1 Model implementation

According to the Scheffé-type model and the number of components q=3 (wood, peat and horse manure), a total run of 7 design points was chosen, as shown in Figure 7. As can be seen, there are no upper or lower limits for the proportions of the three components in this experimental range, except for the only external condition that they must sum to one (Eriksson et al., 1998). In fact, points P1-3-5 represent the pure mixture elements, while points 2-4 and 6 represent the binary mixture (second degree centroids), which has two non-zero components with equal values. Points P7 represent ternary mixtures, which contain all components in equal proportions.

For the analysis of yield, pH and BET, all experiments were performed in triplicate. For the remaining experiments, only P7 was performed in triplicate, while the second degree centroids were performed in single and the pure ones in duplicate. This choice is consistent with performing as few measurements as possible to still obtain a correct statistical result in the model. All the results obtained were analysed using the MODDE software. Thus, an analysis of the effects of each term of the special cubic equation (see Equation 1) was conducted in order to neglect the irrelevant terms.

$$y = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{123} x_1 x_2 x_3 \quad (1)$$

Always using MODDE, an ANOVA analysis was performed to estimate the model likelihood of regression and lack of fit. Finally, the β-coefficients were determined and the predicted values of each trait were plotted.

TABLE 4: List of both single PAH compound concentrations expressed in ng/g and both total PAH concentration expressed in mg/kg according to EBC standards. (1: LOD= 10-50 ng/g and 2: LOD= 50-100 ng/g.).

Sample	Wood	Peat	Manure	MPW	MW	MP	PW
PAH Compound	**[ng/g]**	**[ng/g]**	**[ng/g]**	**[ng/g]**	**[ng/g]**	**[ng/g]**	**[ng/g]**
Naphthalene[1]	3 371	5 464	5 625	6 772	5 383	5 069	5 989
Asenaphtylene[1]	62	60	48	40	40	100	LOD
Asenaphtene[1]	94	96	LOD	78	LOD	86	LOD
Fluorene[1]	49	LOD	LOD	LOD	LOD	70	LOD
Phenanthrene[1]	161	115	808	419	102	462	303
Anthracene[1]	110	96	174	197	76	222	61
Fluoranthene[1]	34	50	66	172	72	158	42
Pyrene[1]	19	49	35	124	44	120	LOD
Benz(a)antracene[1]	73	88	74	214	98	194	842
Chrysene[1]	40	40	61	194	68	170	LOD
Benzo(b)fluoranthene[2]	LOD	LOD	92	261	48	239	LOD
Benzo(k)fluorantene[2]	LOD	LOD	62	141	LOD	157	LOD
Benzo(a)pyrene[2]	LOD	LOD	79	174	75	172	LOD
Benzo(ghi)perylene[2]	LOD	LOD	LOD	94	LOD	116	LOD
Dibenz(ah)antracene[2]	LOD	LOD	LOD	58	LOD	LOD	LOD
Indeno(1,2,3-cd)pyrene[2]	LOD	LOD	LOD	89	LOD	110	LOD
ΣPAHS [mg/kg]	4,0	6,1	7,1	9,1	6,0	7,4	7,2

4.2 Model Results and Discussion

The predicted values of the main biochar properties resulting from the Scheffé mixture model are shown in Figure 8. Regarding the plots (A-B-C-D-E-F), almost all properties show a linear dependence on pure mixtures (βi > > βij), only one quadratic term over three was found to be non-negligible for each property compared to the others. The only exception is PAH, where the βij coefficients have a higher value, showing that interactions between all components are relevant and should not be neglected.

Main variables of ANOVA statistical analysis are shown in Table 5. In the table:

n represents the number of observations considered for the model

$R^2 = {SS_{reg}}/{SS_{tot}}$ represents the goodness of fit

$SS_{reg} = \sum(\hat{y}_i - \bar{y})^2$ regression sum of squares explained by the model

$SS_{tot} = \sum(y_i - \bar{y})^2$ total sum of squares

$R^2_{adj} = 1 - \frac{{SS_{reg}}/{(n-p)}}{{SS_{tot}}/{(n-1)}}$ represents the adjusted goodness of fit

The quality of the generated models can be seen in both Figure 8 and Table 5, where a good agreement between predicted and observed value (R^2 close to one) can be observed for almost all characteristics. Furthermore, almost all models are statistically good, as the regression probability is close to zero (regression < 0,005). Only for the properties SSA and Yields the fit is insufficient as the p-value is close to zero. This SSA value is mainly due to the inherent properties of the machine BET.

TABLE 5: Relevant ANOVA statistic values for each modelled property.

Property	n	R^2	R^2_{adj}	$p_{regression}$	$p_{lack\text{-}of\text{-}fit}$
C	11	0,945	0,932	<0,005	0,147
H	11	0,924	0,891	<0,005	0,523
S	10	0,889	0,852	<0,005	0,116
pH	19	0,944	0,928	<0,005	0,182
SSA	19	0,993	0,992	<0,005	0,008
Yield	19	0,94	0,856	<0,005	0,026
PAH	11	0,800	0,600	0,077	0,230

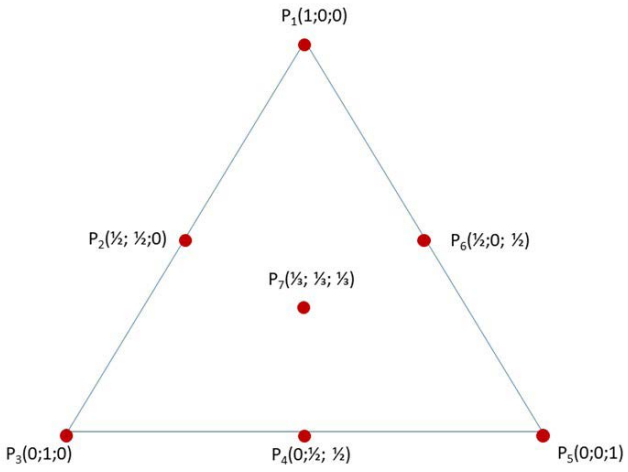
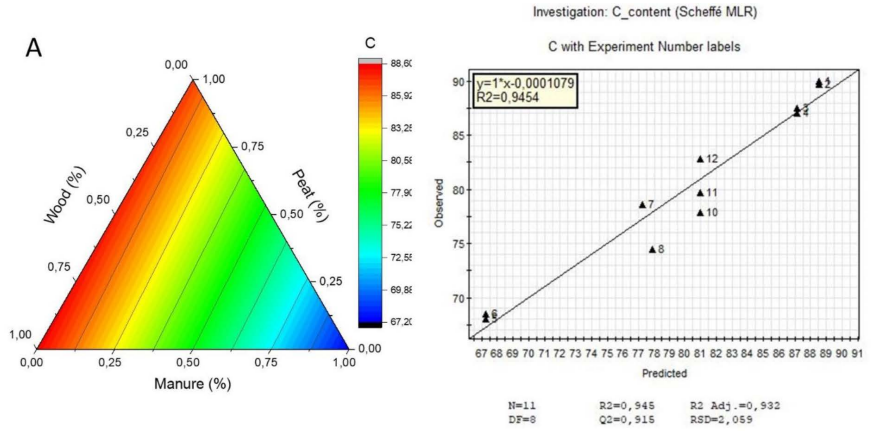
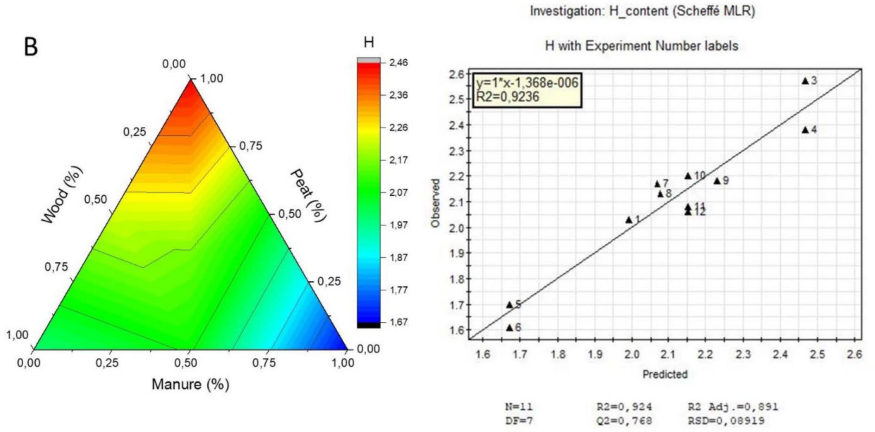
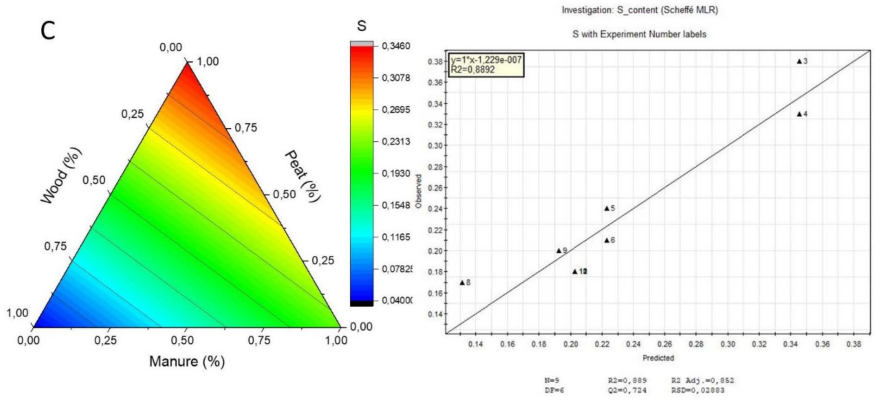
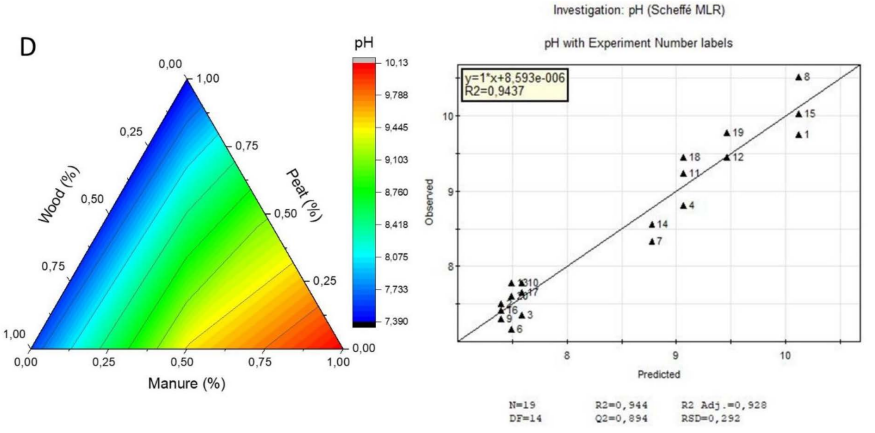


FIGURE 7: Representation of the selected design points for the mixture model.


A
C
Wood (%)
Peat (%)
Manure (%)
Investigation: C_content (Scheffé MLR)
C with Experiment Number labels
y=1*x-0,0001079
R2=0,9454
Observed
Predicted
N=11
DF=8
R2=0,945
Q2=0,915
R2 Adj.=0,932
RSD=2,059


B
H
Wood (%)
Peat (%)
Manure (%)
Investigation: H_content (Scheffé MLR)
H with Experiment Number labels
y=1*x-1,368e-006
R2=0,9236
Observed
Predicted
N=11
DF=7
R2=0,924
Q2=0,768
R2 Adj.=0,891
RSD=0,08919


C
S
Wood (%)
Peat (%)
Manure (%)
Investigation: S_content (Scheffé MLR)
S with Experiment Number labels
y=1*x-1,229e-007
R2=0,8892
Observed
Predicted
N=9
DF=6
R2=0,889
Q2=0,724
R2 Adj.=0,852
RSD=0,02883


D
pH
Wood (%)
Peat (%)
Manure (%)
Investigation: pH (Scheffé MLR)
pH with Experiment Number labels
y=1*x+8,593e-006
R2=0,9437
Observed
Predicted
N=19
DF=14
R2=0,944
Q2=0,894
R2 Adj.=0,928
RSD=0,292

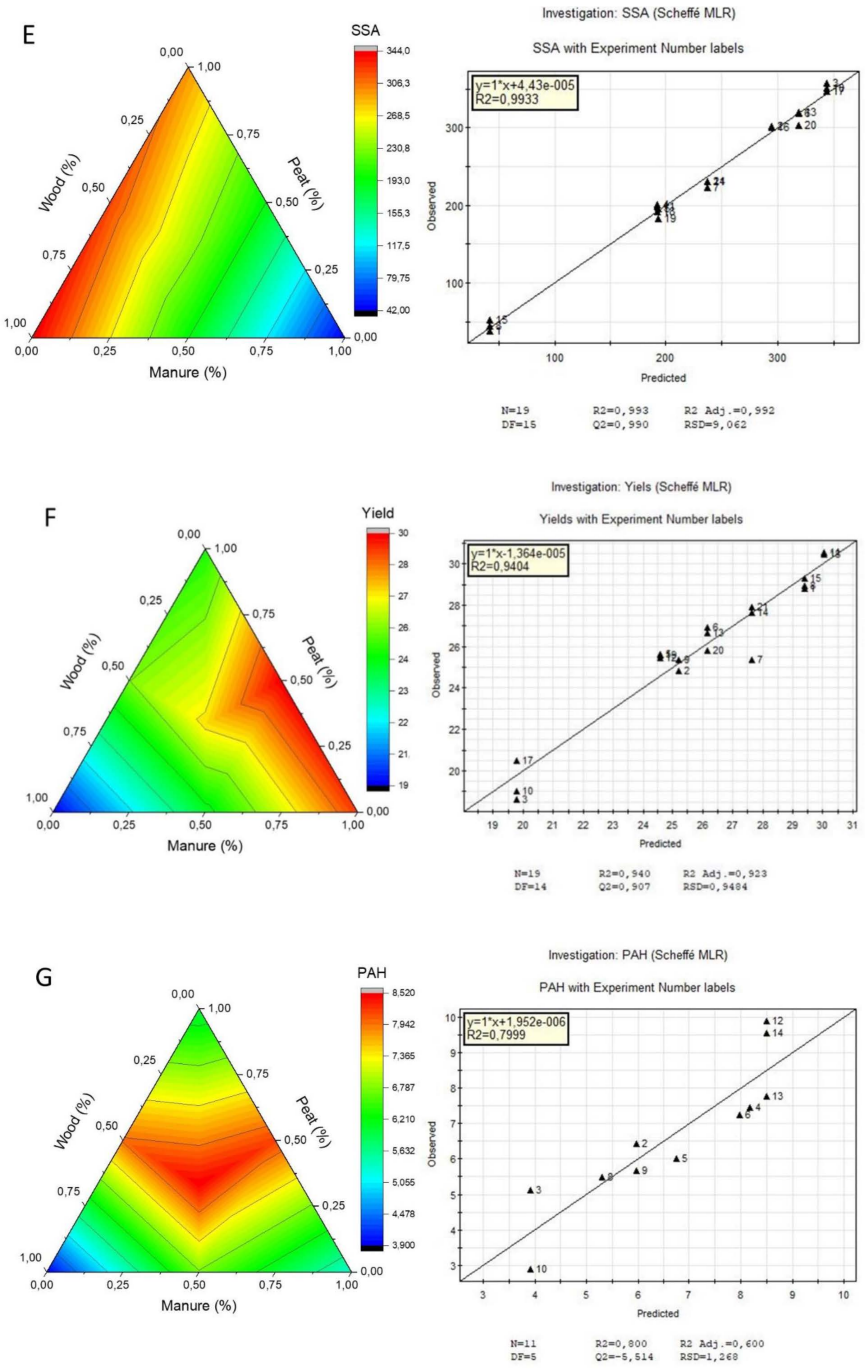


FIGURE 8: Contour plot of predicted values (left) and plot of measured values versus predicted values (right) (Values for C, H, S, and yield are in [%], while SSA [m^2/g], PAH [mg/kg], and pH are pure numbers).

The only property for which no mixture model was found is PAH, as it has the lowest coefficient of determination (0,8) and is statistically poor (regression = 0,077). In fact, the behaviour of PAH is not fully understood. In order to find some possible correlations between PAH and all the other properties studied, a correlation matrix was created using MODDE. The results of this analysis are shown in Figure 9, where PAH has a weak negative correlation with SSA (-0,37) and PV (-0,40) and a weak positive correlation with manure (0,32). It was assumed that SSA and PV or the surface functional groups are the most likely properties to explain the behaviour of PAH. The principal component analysis (PCA) also did not explain the trend of PAH very well. However, this may indicate that variables with a strong influence on PAH are not present in the data set studied. These results suggest that more in-depth studies of the PAH formation mechanism and interaction with porous materials are needed.

5. CONCLUSIONS

A range of detailed information was provided to verify the quality of the produced biochar and its applicability.

The results of proximate and CHNSO analysis show that the biochar produced has less variation in elemental composition compared to the original biomass. In particular, the carbon content of all products is greater than 50%, allowing the char produced to be classified as 'biochar' in accordance with the main voluntary biochar product standards (EBC, Biochar Quality Mandate (BQM) and International Biochar Initiative Standard (IBI-BS). Greater variation in specific values depending on the choice of feedstock was found in the analysis of pH, PAH and BET. In particular, the results of the BET analysis show that woody and peaty biochar have higher SSA values, namely more than 181 m^2/g in each sample where at least one of the two substances is present. In addition, manure biochar has a higher percentage of macropores, resulting in a lower SSA value (only 45 m^2/g). pH results show how pyrolytic conversion increases this value enormously, as all biochar produced is classified as alkaline. The PAH analysis shows that all the biochar can be applied to the soil as its value is below the threshold of 12 mg/kg according to the EBC criteria (Schmidt et al, 2021). The results of the pH, PAH and BET analyses indicate that biochar can be used as a soil amendment: a high pH can prevent the problem of soil acidification, a PAH concentration below the limit does not pose a risk to human health, and a high SSA and PSD variation provides habitat for microorganisms and reduces GHG emissions in the soil. The shape of the original feedstock is retained after the pyrolysis process. This is not the case for volume, which is significantly reduced. This reduction is particularly evident in the case of woody materials, where the volume of biochar is halved compared to the biomass. This phenomenon has positive implications for waste disposal. The application of the mixture model to the experimental data showed how mixtures subjected to pyrolysis behave as physically bounded materials. Using this approach, it was possible to predict the response of key properties for any combination of constituents and calculate the influence of each component on the final value, with very good agreement between estimated and observed values. This could also be useful on an industrial scale to predict what the final biochar will look like, or to adjust the properties of the final product to a good approximation. This result suggests that this type of approach could also be applied to other types of organic residues. The only exception was the PAH content. It was found that this property does not behave as a function of the mixture components, as the concentrations in mixtures are higher than in pure materials. Further analysis and studies are needed to gain a better understanding of the behaviour of the PAH content and the mechanisms of its formation. Research on the pyrolysis of mixed organic materials can serve as a basis for future studies in the field of organic waste recycling and disposal. For instance, the disposal of municipal and agricultural effluents. These materials are difficult to pyrolyse due to their high moisture content and low carbon content, but when mixed with other biomass can produce reusable products for the agricultural and industrial sectors.

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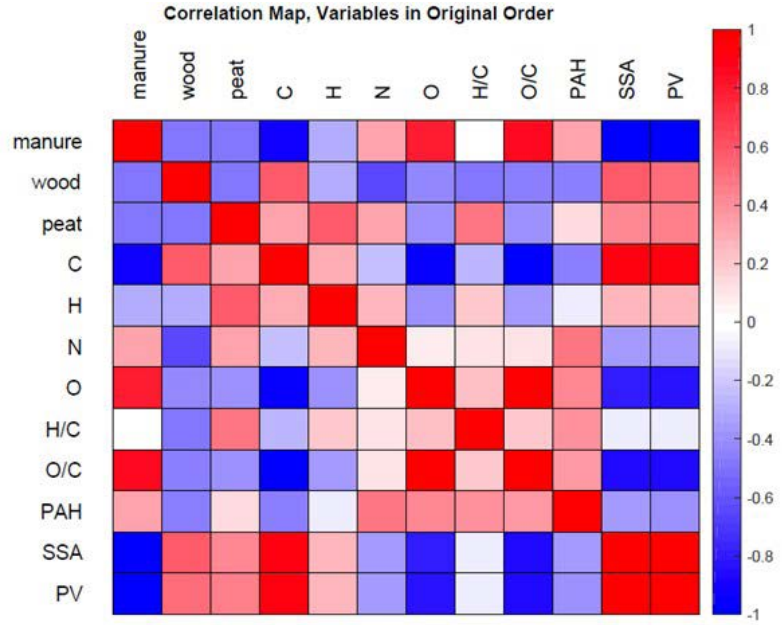

FIGURE 9: Correlation matrix among all investigated biochar properties.

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ADVANCES IN UNDERSTANDING KINETIC MECHANISMS UNDERLYING WASTE GROUND TYRE RUBBER PYROLYSIS

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ABSTRACT

The depletion of natural resources and the need to reduce solid waste in urban areas have necessitated the incorporation of used materials such as waste ground tyre rubbers (WGTR), into manufacturing processes. As a result, techniques and recycling methods have been established to use tyres as feedstock for marketable products since tyres have a calorific value higher than coal and contain a significant amount of carbon black. Among several techniques, pyrolysis has emerged as the most appealing for treating WGTRs. This technique allows the recovery of valuable products like combustible gases, fuels and chemicals, and activated carbon. Studies have focused on understanding the mechanism underlying the WGTR pyrolysis through the establishment of mathematical models and reaction patterns to valorise WGTRs and efficiently produce marketable chemicals. This paper presents an overview of recent developments in understanding WGTR pyrolysis mechanisms. A general mechanism observed involves a first depolymerisation/condensation of the rubbers, then a degradation of the condensed products, and finally a devolatilisation of additives. Based on the limited information available on the chemicals' formation mechanism, it is assumed that limonene and isoprene are derived from natural rubber (NR), through a series of β-scission and depropagation reactions of polyisoprene and intramolecular cyclisation and scission of monomeric isoprene, respectively, with an equilibrium step of Diels-Alder reaction. The maximum yield of limonene and isoprene have been found to be 51% and 20.5% at temperature around 500°C respectively. The isoprene yield can be increased up to 37.57 % with the use of catalyst such as Calcium Oxide.

1. INTRODUCTION

Renewable sources and waste valorisation processes are gaining interest due to several factors, including eliminating global warming and society's significant dependence on the limited fossil sources for fuels and essential raw materials. Moreover, the remarkable increase in the number of vehicles worldwide coupled with the inadequate technical and economic waste tyres recycling methods have led waste tyres to be considered one of the severe pollution problems in waste disposal (Martinez et al., 2013).

However, the world market for light vehicles is increasing steeply. In 2018, the global production of motor vehicles was 98.1 million units, with the future growth estimated at 110 million units by 2025. Accordingly, the demand for tyres will also increase, imposing a significant challenge to reuse or dispose of this complex material after use (Association, 2019; Menares et al., 2020). The annual global increment of waste tyre is estimated to around 17 million tons, and it is expected to reach 1.2 billion tons per year by the late 2030s (J. Xu et al., 2021).

Tyres are made of 38% rubber, 30% fillers (carbon black, silica and carbon chalk), 16% reinforcing material (steel, rayon, nylon), 10% plasticizers (oils and resins), 4% vulcanisation agents (sulphur, zinc oxide, various chemicals), 1% antioxidants to counter ozone effect and material fatigue and 1% of miscellaneous (Nkosi & Muzenda, 2014). On the other hand, waste tyres (WT) is a problematic waste that belongs to a type of solid waste named "bulky" in waste management. They refer to tyres that have exceeded their useful lifespan in roadworthiness and are difficult to degrade under typical environmental conditions (Q. Chen et al., 2022; Ishola Felix et al., 2018). The need to reduce solid waste in cities and the depletion of natural resources have necessitated the incorporation of scrap material into productive processes; hence giving value to what would oth-

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erwise be deemed waste and reducing the consumption of natural resources (Ramirez-Canon et al., 2018).

Therefore, researchers have been interested in developing processes and recycling strategies for waste tyres. These strategies aim at reducing waste tyre effects on the environment and take advantage of them as feedstock for marketable products since they have a calorific value higher than coal and a considerable amount of carbon black when the char is significantly refined. Waste tyre management methods may be classified into three categories: i.e., i) direct disposal (landfilling and stockpiling); ii) material recovery and recycling (milling/grinding, re-treading, devulcanisation and civil engineering applications); and iii) thermal treatment with energy recovery (incineration, gasification and pyrolysis) (Isayev, 2005; Rowhani & Rainey, 2016; Viglasky et al., 2017).

Waste tyres thermochemical conversion is one of the attractive processes used for valorisation or disposal. Incineration and combustion of waste tyres are beautiful solutions for heat and power production in conventional coal-based plants. However, these processes are deemed inefficient since they do not cater for valuable product recovery from the different fractions of the tyres (rubber, metal, carbon black) (Menares et al., 2020).

The thermochemical process of gasification is a sub-stoichiometric oxidation of organic material. The process involves the use of air, oxygen, hydrogen or steam/water as a reaction agent. Despite the considerable variation of the process, typical gasifiers operate at temperature between 700 and 800°C and its energy efficiency is reported to be around 76% (Viglasky et al., 2017).

A technically attractive way and most promising recycling strategy for the thermochemical treatment of WTs that allows the recovery of valuable products such as combustible gases, fuels and chemicals and activated carbons is pyrolysis (Q. Chen et al., 2022). Pyrolysis is a process of thermally decomposing the organic volatile matter of tyres (mainly the rubber polymers) into low molecular weight products, liquids or gases (Aylón et al., 2010).

WT pyrolysis techniques can be classified into several types depending on the operating parameters, such as the heating rate, the volatile residence time and the temperature. A simple classification comprises a slow pyrolysis, fast pyrolysis and a catalytic pyrolysis.

Slow pyrolysis considers a slow pyrolytic decomposition at low temperatures and is characterised by low heating rates, relatively long solid and vapour residence times (in order of minutes to hours). The longer residence times lead to secondary conversion of primary products, yielding more coke, tar, as well as thermally stable products. The primary objective of this type of pyrolysis is the char production, although tar and gases are also obtained (Martínez et al., 2013).

Unlike the slow pyrolysis, fast pyrolysis implies a rapid thermal decomposition and is characterised by higher heating rates. The process usually requires a feedstock with small particle sizes and devices with special design to allow removing the vapours released quickly. The fast pyrolysis is recognised as an effective conversion route for the production of liquid fuels, chemicals and derived products with higher yield, generally favoured by high heating rates with short hot zone residence times and rapid quenching of the volatile products (Martínez et al., 2013).

Catalytic pyrolysis refers to any pyrolytic process that comprises a catalytic material in the same process in order to favour or upgrade some yield or properties of the products. WGTR catalytic pyrolysis has been conducted for the production of single ring aromatic compounds in the liquid fraction such as benzene, toluene and xylenes (Martínez et al., 2013).

The WGTRs pyrolysis products include a pyrolysis oil (tyre-derived oil, TDO) which is the most important fraction for energy recovery (engine fuels) and recovery of valuable chemical products such as limonene, benzene, toluene, xylene (BTX). Additionally, gas and solid are also obtained, being the first used to fulfil the energy requirements of the pyrolysis process. While the solid product, also known as char, can be used for producing carbon black or activated carbon as an additive for improved asphaltic and concrete mixtures and can be applied in tyre manufacturing (Ma et al., 2020; McCullough et al., 2015; Menares et al., 2020).

Albeit pyrolysis of wastes appears simple in concept, the products are often low-value mixtures of hydrocarbons with an extensive compositional range, sometimes extending from light gases to coke. The composition of different pyrolysis products depends on the conditions used and on the composition of the tyre. For this reason, depending on the final objective of the pyrolysis, it is necessary to find the optimal conditions for the type of feedstock and the process operating parameters (B Acevedo & Barriocanal, 2015; Martínez et al., 2013).

Several researchers investigated the influence of WGTR pyrolysis parameters on the devolatilisation of rubber components pathways. These parameters include temperature, pressure, particle size, inert gas flow rates, types of pyrolysis atmospheres, reactor configuration and the use of catalysts. However, no general agreement could be found among these studies on the relationship between products yields and these parameters (Parthasarathy et al., 2016; Quek & Balasubramanian, 2012).

Researchers have used the pyrolysis of solid-state materials mechanisms in the endeavour of the valorisation of the waste tyre. The approach entails developing appropriate mathematical models and reaction patterns from the thermogravimetric analyser (TGA) data, a typical thermal method of material analysis. Hence, different models have been used, including kinetic, mass transfer, and heat diffusion models (Khiari et al., 2018).

The state of the art of waste tyre pyrolysis process was reviewed for the first time in literature by Martínez et al. (2013). They presented a comprehensive review of the process by stating the effects of the primary process conditions, including the size and composition of the feedstock, on the distributions and physicochemical properties of the pyrolysis products (gas, liquid and solid fractions).

Moreover, they pointed out the main properties of the pyrolytic products with special attention given to liquid fraction by highlighting its properties as an alternative fuel in compression ignition engines. However, Williams (2013), in their review of the pyrolysis process of waste tyres, pre-

sented the range of reactors used so far by pointing out the influence of the reactors on the product yield and gas and oil composition. They also showed the principal gases produced from the pyrolysis of waste tyres to be H_2, C_1 - C_4 hydrocarbons, CO_2, CO and H_2S. In addition, they reported on the upgrading of char to higher quality carbon black and activated carbon. They also used catalysts to upgrade the oil to an aromatic-rich chemical feedstock or hydrogen from waste tyres. Nkosi and Muzenda (2014) also presented a review of the pyrolysis process by highlighting the influence of the operating conditions and discussing the pyrolytic products. Moreover, they analysed the pyrolysis products market and the success and failures of the process.

J. Singh (2015) reviewed and discussed the tyre pyrolysis process and the applications of the derived products. They reported the characteristics of used tyres materials and recycling methods, the types and principles of pyrolysis, the pyrolysis products and their composition, concluding by the advantages of a waste tyre pyrolysis plant. Lewandowski et al. (2019) discussed the current use of different pyrolytic reactors, their constructions and operating principles regarding the yields of main products of waste tyre pyrolysis. They summarised and compared main products yields (oil, gas, coal) obtained in different reactors and by different authors. Januszewicz et al. (2020) also conducted a review on the technologies of limonene production from waste tyre pyrolysis. They showed that the conditions that facilitate increasing limonene yields (low temperature and pressure, fast heating rate and short residence time of volatile products in the reaction) are best obtained in the following reactors: Vacuum mechanical, fixed bed, inert gas and catalyst, fluidised bed and mechanical pyrolizers being the least efficient.

Recently, Jahirul et al. (2021) investigated the use of waste tyres as an alternative fuel to address the global problem of waste tyre management and environmental concerns. They reviewed recent publications on the topic and found that pyrolysis is the most common thermochemical method for addressing the waste tyre management issue due its simplicity, high recovery of liquid and solid materials, and low environmental impact. They concluded that the product yield and composition of waste tyre depends n reactor type and operating condition. The average production yield, char, syngas, and steel from waste tyre pyrolysis is 40-60%, 10-20%, and 10-15% by weight, with the favourable temperature range for the high yield of liquid oil being 450-500°C. Mavukwana and Sempuga (2022) also conducted a review on the analysis of the recent advances in waste tyre pyrolysis and gasification technologies. They concluded that a techno-economic analysis to compare the use of gasification/co-gasification of waste tyres with other solid-to-liquid processes is required, and that a solar assisted pyrolysis could offer energy/cost savings opportunities.

From the above, since pyrolysis of waste tyres has received particular attention in the 1990s, the kinetic theory was still in a state of considerable disarray and the devolatilisation mechanisms for tyre pyrolysis, in their formative stages. Since then, understanding the reaction dynamics involved in pyrolytic processes has evolved substantially, and the corresponding kinetic schemes have been refined to fully describe the entire tyre pyrolysis process. In light of this, this paper intends to provide a concise overview of the advances in understating the mechanisms underlying the waste tyres pyrolysis process.

In addition, this paper will review waste tyre pyrolysis in terms of the composition of the products from the pyrolysis process. The waste tyre pyrolysis mechanisms are presented in detail. The research related to the pyrolysis kinetics and modelling approach is also reviewed and discussed.

2. WASTE TYRE PYROLYSIS

2.1 Process description

Pyrolysis consists of a thermal decomposition of organic materials without oxygen, cracking them down to simpler organic compounds. It relies on the addition of heat to break chemical bonds, providing a mechanism by which organics decompose and vaporize. Most tyre pyrolysis processes operate within a temperature range of 250-500°C, although some are reported to run at up to 900°C. At temperatures above approximately 250°C, shredded tyres release higher amounts of oil and gases. In contrast, above 400°C, oil and solid tyre-derived char yield may decrease relative to gas production (Antoniou & Zabaniotou, 2013).

The rubber is heated in the reactor and consecutively, the rubber polymers break down into smaller molecules which eventually evaporate and exit from the reactor. These hot volatiles can be burned directly to produce power or condensed into an oily type liquid, called pyrolysis oil or bio-oil. Smaller molecules, unable to condense, remain as a gas and are burned as fuel. The minerals contained in the tyre, such as sulphur, zinc oxides etc., are removed as a solid (Viglasky et al., 2017).

A tyre pyrolysis process is an endothermic process. Thus, temperature exerts a remarkable effect in the products and conversion grade. If the temperature is around 450°C, the main product is liquid, a mixture of hydrocarbons depending on the waste material's initial composition. At a temperature above 700°C and due to further cracking of liquids, a mix of hydrogen and carbon monoxide (synthetic gas) becomes the primary product (Viglasky et al., 2017).

Thus, the nature of the feedstock and process conditions defines the properties of the pyrolysis products. For example, whole tyres contain fibres and steel, while shredded tyres have most steel, and sometimes most of the fibre removed. In addition, the reactor is an essential part of the pyrolysis process. Researchers have used a wide range of reactors, including fixed-bed (batch), fluidized-bed, rotary kiln, screw kiln, and spouted bed for scrap tyre pyrolysis (Lewandowski et al., 2019; Rowhani & Rainey, 2016; Viglasky et al., 2017). The process can be batch or continuous, according to pressure applied, i.e., at atmospheric or vacuum. The energy required for thermal devolatilisation of the scrap tyres can be in the form of directly-fired fuel, electrical induction and or microwaves. The process uses nitrogen or another inert gas as carrier gas. To some extent, the pyrolysis might require a catalyst to accelerate the process (Viglasky et al., 2017).

Pyrolysis products are gas, liquid and char. The liquid is the highly regarded and economically valuable fraction for its high heating value (>40 MJ/kg) and high-value chemicals (Q. Chen et al., 2022; Hita et al., 2016). Therefore, the most profitable reactor designs and process operating parameters allow higher liquid yields. A schematic of the WT pyrolysis process is shown in Figure 1.

The liquid fraction also called pyrolysis oil includes a wide range of compounds, such as alkanes, alkenes, aromatic compounds, and hydroxyl compounds (G. Zhang et al., 2021). Therefore, the tyre pyrolysis oil is a potential source of fuel and chemicals. The specific chemicals are separated from the bulk tyre oil through several techniques and depending on the composition and properties of the oil. The Most useful techniques are distillation, the widely used technique and most effective for separating volatile hydrocarbons form the oil, solvent extraction that involves the use of a solvent to selectively dissolve and extract certain components from the bulk tyre, fractional crystallisation that exploits the difference in solubility of components in a solution, adsorption that involves the attachment of certain components of the bulk tyre oil onto a solid surface known as an adsorbent, membrane separation that uses semipermeable membranes to separate components based on their size, polarity, or other properties, and, centrifugation that involves the use of centrifugal force to separate components based on their density (Drugkar et al., 2022; Farzad et al., 2021; Gollakota et al., 2016; Januszewicz et al., 2020; G. Zhang et al., 2021).

2.2 Operating parameters

WT pyrolysis is an endothermic process maintained by temperature in the reactor. Temperature emerges as the operating parameter that exerts a considerable effect on the product distribution and conversion grade.

Therefore, temperature is the parameter that significantly influences the pyrolysis process and the WGTR pyrolysis mechanisms. The heating rate and particle size interact in the heat transfer phenomena directly with the gas, liquid, and solid fraction distribution and their physicochemical properties (Martínez et al., 2013). The carrier gas flow and the atmosphere type also have a considerable effect in the process, controlling the occurrence of secondary pyrolysis reactions such as thermal cracking, repolymerisation, recondensation and/or char formation (Martínez et al., 2013). Other parameters such as pyrolysis time and hot volatiles residence time involved in the process also exert a remarkable effect.

Three phases are obtained from the WGTR pyrolysis process: solid, liquid, and gas. Their composition is related to the temperature of the thermal treatment. In addition, from the conversion point of view, 500°C appears to be the optimum temperature at atmospheric pressure since total tyre conversion is achieved (Aylón et al., 2005; M.F. Laresgoiti et al., 2000). The principal tyre compounds (NR, BR and SBR) remain in the pyrolytic carbon black at lower temperatures, showing a heterogeneous sticky-gummy feature (Martínez et al., 2013). At higher temperatures, there are no reported significant influence on the amount and characteristics of the pyrolysis products (González et al., 2001; M. F. Laresgoiti et al., 2000).

Gas yield increases with temperature due to substantial thermal cracking at high temperatures (Zabaniotou & Stavropoulos, 2003). Gas compounds and yields are susceptible to secondary reactions and heterogeneous reactions involving the inorganic compounds of a tyre. Therefore, the gas fraction behaviour in terms of composition, calorific value and yield are quite disparate among results reported in the literature (Martínez et al., 2013). It is expected that longer chain hydrocarbons decrease as temperature increases in favour of lighter hydrocarbons and H_2.

On the solid fraction, no significant changes in the yield are expected when pyrolysis temperature increases. Therefore, the amount of the solid fraction must be similar to the sum of the original char and the ash content. However, due to secondary reactions such as tar and char formation reactions, the solid fraction can be higher than the expected value. On the contrary, when the carrier gas has some oxygen content (CO_2 and/or steam), an increase in temperature can also promote a lower char yield, given the occurrence of gasification reactions (Betancur et al., 2009; Martínez et al., 2013).

However, the liquid yield of pyrolysis is almost stable or shows a maximum at around 450-500°C and decreases

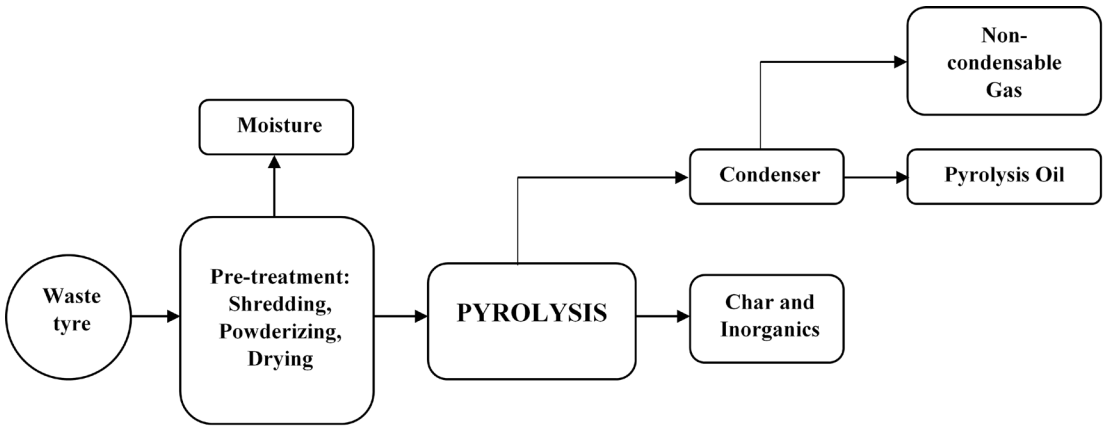

FIGURE 1: Waste tyre pyrolysis process schematic.

at higher temperatures. Simultaneously, the aromatic compounds in the liquid fraction increase. The increase in aromatic compounds is due to secondary reactions that modify the chemical properties and yields of the products, as mentioned previously on the influence on the gas products. Moreover, F. Xu et al. (2018) reported that the primary pyrolysis products of gases, alkenes and aromatics greatly vary when the temperature changes. The fraction of alkenes decreases with temperature increase due to secondary cracking of pyrolysis products in the temperature range of 600-800°C and then increases when the temperature reaches 800°C and above.

The yield of limonene, one of the alkenes' main products, increases at higher temperatures (around 450°C) and decreases when the temperature reaches 800°C. The decreasing of limonene content is attributed to the decomposition of D-limonene into aromatics due to secondary reactions such as cyclisation and aromatisation at high temperatures (N. Mkhize et al., 2016; F. Xu et al., 2018). However, the content of D-limonene shows an increase when the temperature is raised from 800°C to 1000°C due to some reactions such as the Diels-Alder reaction of isoprene (F. Xu et al., 2018). Sanchís et al. (2022) confirmed the influence of temperature profile on both the distribution and properties of products, when investigating the effect of different temperature profiles by using a single-auger pyrolysis reactor in an industrially relevant scale and two temperature profiles (425-550-775°C and 600-700-800°C). They found that the 425-550-775°C profile enhanced limonene production, while the raise of temperature favoured the production of single-ring aromatics, particularly benzene, toluene, ethylbenzene and xylenes in TDO.

The previous observation was made for another chemical of tyre oil, i.e., indene. The yield of indene shows an increase with temperature increase up to 500°C then decreases at higher temperatures.

Next to temperature, heating rate plays a vital role in controlling the product yield of pyrolysis. An increase in the heating rate shifts to higher temperatures the weight loss profile in the thermogravimetric analysis. Leung and Wang (1998) reported that with increasing heating rate, the weight loss regions shift to a higher temperature range, the weight loss rate increased and the reaction time shortened quickly with no noticeable change in the total weight loss. The apparent activation energy and frequency factor also increase with increasing heating rate, increasing the pyrolysis reaction's difficulties.

Pressure is another parameter that influences the production of chemicals from pyrolysis. Decreasing the pyrolysis pressure leads to a decrease in the residence time (Roy et al., 1997). Hence, the formation of undesired products and the destruction of desirable chemicals, such as limonene, are minimised. Roy et al. (1997) found that dl-limonene decreased with increasing pyrolysis pressure. Therefore, it is preferable to perform rubber pyrolysis at low pressures to produce chemicals of higher commercial value. Ma et al. (2020), while studying the effect of residence time and pressure on limonene at pressurized pyrolysis of waste tyre, found that, at the constant residence time, pressure exhibits a positive effect on limonene production. The yield of limonene was found to increase by 73% and limonene concentrations in TDO increased by 60%, as the pressure increased from 0.1 MPa to 1.0 MPa and at a constant residence time of 30 s.

In an effort to improve the quality of the products and the selectivity of the WT pyrolysis process, the use of catalysts has merged as an interesting alternative. The catalysts contribute to increased yields of valuable aromatic compounds, improve the quality of the resulting products, such as TPO, and help reduce the presence of sulphur-containing compounds. They enable the conversion of waste tyres into more valuable chemical products, thereby enhancing the economic and environmental aspects of waste tyre disposal (Miriam Arabiourrutia et al., 2020; Williams, 2013). A wide range of catalysts have been proposed in the literature for WT valorisation, with zeolites being the most commonly used due to their capacity for the production of valuable chemicals, such as BTX and light olefins (Miriam Arabiourrutia et al., 2020). Notable microporous acid zeolites used include HZSM-5 and HY, with differences in pores sizes influencing their selectivity. HZMS-5 favours monomolecular cracking, while HY has a higher aromatization capacity due to its higher acid density (Rowhani & Rainey, 2016; Williams, 2013). Other zeolites like Hβ, HZSM-22, HMOR, SAPO-11, and ZSM-22 have been explored for tyre pyrolysis. Their varying pore structures and acidities contribute to different product distributions, with some favouring gas and aromatic production (W. Li et al., 2016; Muenpol et al., 2015). Base catalysts, while less active than acid catalysts for C-C bond cleavage, facilitate hydrogenation, isomerization, alkylation, and reactions involving heteroatoms. MgO and CaO are commonly used base catalysts for tyre pyrolysis, improving the quality of the liquid and enhancing cracking activity (Kordoghli, Khiari, et al., 2017; Kordoghli, Paraschiv, et al., 2017; Shah et al., 2008). Carbonates, hydroxides, and natural materials like dolomite, olivine, and red mud have also been tested. Some of these materials, like dolomite and olivine, exhibit sulphur removal capabilities, resulting in TPO with low sulphur content (Choi et al., 2016; Demirbas et al., 2016; X. Zhang et al., 2008).

Different reactor configurations have been employed for catalytic pyrolysis, including fixed bed batch reactors, bench-scale units (fluidized beds, spouted beds, and rotary reactors), and pilot plant-scale systems operating under continuous fast pyrolysis. The catalysts were placed either in situ or ex situ in a second reactor (Miriam Arabiourrutia et al., 2020). However, the majority of studies are at the preliminary or laboratory scale. In the in situ catalytic pyrolysis, the catalyst is placed within the same reactor as the pyrolysis process. San Miguel et al. (2006) conducted an experiment where they integrated in situ zeolites into a thermobalance sample container coupled to a GC/MS. They observed that these catalysts exhibited a significant preference for producing BTX, while simultaneously reducing olefinic hydrocarbons. In the ex situ method, a second reactor is employed for the catalytic cracking of pyrolysis volatiles, separated from the pyrolysis reactor. Ex situ catalytic cracking of tyre pyrolysis volatile has primarily been studied in fixed bed reactors, with various

configurations been explored (Miriam Arabiourrutia et al., 2020). (Kordoghli, Paraschiv, et al., 2017) investigated the pyrolysis batches scrap at 500°C and the in-line cracking of the stream leaving the first reactor on different catalysts, such as ZSM-5, Al_2O_3, $CaCO_3$ and MgO. They found that $CaCO_3$ was the most influence catalyst. The direct contact of $CaCO_3$ with the tyres led to an augmentation of total conversion from 54.59% to 63.92% in TGA tests, and from 54.9% to 62.7% in bench-scale installation. In contact just with the pyrolysis vapours, the tyre conversion only reached 59.7%. Boxiong et al. (2007) conducted a study involving the batch catalytic pyrolysis of waste tyre using ZMS-5 and USY catalyst. The setup used comprised two fixed bed reactors, with the pyrolysis step conducted at a temperature of 500°C and the subsequent catalytic cracking taking place within the temperature range of 350-500°C. They found that the influence of catalysts was to reduce the yield of oil with a consequent increase in the gas yield and high concentrations of single aromatics. The concentrations of toluene in the light fraction from un-catalysed oil was of 3.04wt%, which increased to 5.68wt% with the ZSM-5 and 13.70wt% with the USY catalyst. Williams and Brindle (2003) also investigated batch pyrolysis of waste tyres at a temperature of 500°C and a subsequent in-line catalytic cracking of the pyrolysis volatiles using HY and HZSM-5 zeolites within the temperature range of 430 to 600°C, to maximise the concentration of single ring aromatic compounds. They observed an increase in the concentration of single ring compounds in the oil, with toluene reaching 20wt%, o-xylene 7wt%, benzene 5wt% and m/p xylenes 20wt%.

Furthermore, Choi et al. (2016) developed an innovative process involving two in-line reactors operating continuously, to produce a pyrolysis oil with a low sulphur content. The initial reactor was an auger reactor where partial degradation of waste tyres occurred at a temperature of 340°C, and the subsequent reactor was a fluidized bed reactor operated at 520°C and using various catalysts, such as dolomite and olivine. They obtained the lowest sulphur content of 0.45wt% using calcined olivine. More recently, Osorio-Vargas et al. (2022) examined the catalytic pyrolysis of WT using noble-meal based catalysts supported on nanostructured titanates nanotubes (NT-Ti). The investigation focused on understanding the product distribution and the yield of valuable hydrocarbons, specifically benzene, toluene, xylene (BTX), and p-cymene. The catalysts employed, denoted M/NT-Ti (with M representing Pd, Pt, or Au), exhibited small nanoparticle sizes ranging from 1.8 to 2.2 nanometers and a uniform pore size distribution due to the textual characteristics of the support material. They found that the catalytic pyrolysis significantly increased the production of monoaromatic compounds, with Pd-based catalyst being the most effective, leading to higher yields of BTX and p-cymene compared to non-catalysed pyrolysis. The catalyst exhibited a bifunctional nature, favouring cyclisation, isomerisation, and aromatisation reactions on both metallic and acidic sites, enhancing catalytic activity. Additionally, the study examined the pyrolysis of individual WT polymers and D,L-Limonene to understand the complex reaction pathways.

Table 1 summarises the influence of pyrolysis parameters on WT pyrolysis reaction mechanism by highlighting differences in products yields and some chemical concentrations from the literature.

3. WASTE TYRE PYROLYSIS MECHANISMS

3.1 Introduction

Pyrolysis is defined as the thermal treatment of WTs under inert conditions to yield pyro-gas, tyre-derived oil (TDO) and pyro-char. TDO is the main pyrolysis product fraction on a weight basis, and as a liquid, it is relatively easy to handle. Therefore, TDO is the most interesting pyrolysis product and a potential source for recovering valuable chemicals. At the same time, the resulting residues can be upgraded to liquid fuels comparable to conventional petroleum-derived products and fuels (N. Mkhize et al., 2019).

As previously mentioned, several studies have been performed to investigate the pyrolysis parameters of WTs to oil. However, no general agreement could be found among these studies on the relationship between oil yields and these parameters.

Hence, the pyrolysis process of waste tyres has been investigated in detail over the decades using numerous approaches by various researchers to understand its kinetics and mechanisms.

For instance, J. Chen et al. (2001) investigated thermogravimetrically the pyrolysis kinetics of passenger car tyre (PCT) and truck tyre (TT) in N_2 for heating rates of 5, 10, 20 and 30°C /min and temperature ranging from 100 to 900°C. They found that the pyrolysis reaction begins with the dehydration and devolatilisation of processing oils, followed by the devolatilisation of natural rubber or butadiene rubber. Using Friedman's method, they also reported the average kinetic parameters of E=147.95±0.21 $kJ.mol^{-1}$, A=(6.295±1.275) x 1010 min^{-1}, and n=1.81±0.18 for the two tyres that they observed to behave similarly in pyrolysis devolatilisation.

In the same way, Iwarere and Mkhize (2019) conducted a kinetic mechanism study of two types of WT (TT and PCT) pyrolysis based on the rubbery fractions devolatilisation at heating rates 10 to 50°C/min. They used two model-free methods (Freidman and Kissinger) and observed that the reaction progress profile of the TT matches that of the PCT, with the gradient of the TT profile being steeper compared to the PCT. Moreover, they reported that the TT profile is characterised by one prominent peak attributed to the natural rubber, the main rubbery fraction of the TT. However, two distinctive peaks were observed in the devolatilisation of the PCT. Peak one was sought to be the NR, whereas peak two was associated with synthetic rubber (BR and SBR). Therefore, the authors concluded that there is a high potential for stepwise pyrolysis of the fractions from tyre rubber, particularly PCT, which may benefit the fractional recovery of the valuable chemicals from the WTs.

Seidelt et al. (2006) showed that tyres are made up of the three main components, i.e., NR (polyisoprene), styrene-butadiene rubber copolymer (SBR) and additives (sulphur, zinc oxide (ZnO), carbon black). The derivative thermogravimetric (DTG) curves of these components in

TABLE 1: Influence of WT pyrolysis parameters on products and chemicals production.

Ref.	Material/ Energetic potential	Reactor configuration	Pyrolysis parameters			Tyre pyrolysis products			Chemicals yields in Pyrolytic oil	
			Temp. / Time	Heating rate	Pressure/ Catalyst	Gas %	Solid %	Liquid %	Limonene %	Indene %
J. A. Conesa et al. (2004)	Tyre (4 mm) NCV: 7671.5 kcal/kg	Fixed Bed	450 750 1000	-	-	- 25.1/ 22.15	35.2/13 37.2/14 37.6/16	37.8/25 10.9/13 <0.01	6.9/4.1 g/kg 0.2/1.1 g/kg -	0.3/0.4g/kg 1.6/1.8g/kg
S.-Q. Li et al. (2004)	Shredded scrap tyres (13-15 mm) LHV: 34923 kJ/kg	Rotary Kiln	450 500 550 600 650	-	-20 to -10 Pa	13.1 13.6 15.5 18.0 18.3	43.0 41.3 39.3 39.3 38.8	43.0 45.1 44.6 42.9 53.7	5.440 1.883 0.419 0.122 0.070	0.831 0.381 0.900 0.447 0.382
M. Laresgoiti et al. (2004)	Car tyre (2-3 cm wide) GCV: 31.8 MJ/kg	Autoclave	300 400 500 600 700	15°C/ min	-	7.6 19.3 17.2 17.6 17.8	87.6 55.9 44.8 44.2 43.7	4.8 24.8 38.0 38.2 38.5	21.07 8.22 5.12 3.19 3.29	0.77 0.43 0.90 0.64 0.60
Rofiqul et al. (2007)	Heavy automotive waste tyre (2, 4 and 12 cm^3) HHV: 33.30 MJ/kg	Fixed-bed fire-tube heating reactor	425 475 525 575	15°C/ min optimal	Slightly above the atmospheric	8 9 12.5 18.6	39.5 37 35.5 33	52 55 51 48	50.8 50.86 24.84 21.24	-
M Arabiourrutia et al. (2007)	Scrap car tyres (0.63- 1 mm)	Conical spouted bed reactor	425 500 550 610	-	-	0.70 3.50 3.05 3.18	34 34	30.48 29.30 27.29 23.70	23.93 16.94 13.59 6.34	0.46 1.94 1.15 1.40
G. Lopez et al. (2010)	Tyre (3 g/min) HHV: 38.847 kJ/kg	Conical Spouted Bed	425 600			~2 ~7.5	33.9 35.8		19 <1	-
Islam et al. (2011)	Waste Truck tyre (4 cm^3)	Fixed Bed	375 425 475 525 575	-	-	7.5 8 9 12.5 18	45 39 36 35 35	47 53 55 52 47	50.86	-
Bajus and Olahová (2011)	Automotive scrap tyres (1-3 cm^2) HHV: 38.847 kJ/kg	Batch reactor	450 570	16.5, 9 and 7.5°C/ min	-	11.1 9.3	46.3 40.7	42.6 50.0	9.0 4.6	-
Beatriz Acevedo and Barriocanal (2014)	Tyre crumbs	Rotary Oven Fixed bed	850 850	5°C/min	-	35 3.5	28 38	25 55	5.12 21.58	9.74 3.85
Alvarez et al. (2017)	Waste truck tyre (2.8- 3.3 mm) HHV: 38.2 MJ/kg	Conical spouted bed reactor	425 475 575	10^3-10^4°C/s	-	3.7 5.9 10.1	37.9 35.9 35.9	58.4 58.2 54.0	21.05 22.84 7.04	0.26 0.30 1.09
Song et al. (2017)	Tyre rubber powder (0.6 mm) LHV: 40235 kJ/kg	Microwave	10 20 30 mins	-	-	9.4 11 12	54 44.8 43	36 44 45	8.61 9.92 9.83	1.01 1.47 1.58
R. K. Singh et al. (2018)	LVT MVT HVT	Batch reactor	650 750 750	20°C/ min	Max 3 atm	8.5 12 9	39 42 27	51 45.5 63.5	11.11 21.22 12.75	0.45 0.80 0.44
Ma et al. (2020)	TT Powder	Fixed-bed	500	20°C/ min	0.1MPa 1.5MPa		33 53	45 32	6.69 6.75	-
Williams and Brindle (2002)	Used tyres 1.0-1.4mm	2 Fixed beds	500/ 430	10°C/ min	ZSM-5 HY	15.1 16.8	38 37.3	42.9 38.7	-	-
Shah et al. (2008)	Tyres 5 10 mm	Fixed Bed	400 400	5°C/min	MgO $CaCO_3$	19.3 31.9	53.5 38.9	27 29.2	-	-
Miandad et al. (2018)	WT granules (2-3.5mm)	Pilot scale reactor	450	10°C/ min	No-catalytic Nat. Zeolite H-SDUSY Al_2O_3 $Ca(OH)_2$	20.0 24.6 37.4 34.1 18.4	40.0 53.4 42.6 33.9 55.6	40.0 22.0 20.0 32.0 26.0	-	-

the proper ratios were superimposed on DTG curves of tyres under study through a trial-and-error process. The author performed a similarity merging to show a good agreement with experimental results using kinetic parameters obtained for each component. B Danon et al. (2015) investigated the pyrolytic devolatilisation behaviour of four rubbers (NR, Synthetic polyisoprene, BR and SBR) at five heating rates (2, 5, 10, 15 and 20°C/min), using combined model-free and model-based kinetics. They concluded that the devolatilisation of the four rubbers consisted of two separate zones of weight loss (devolatilisation reactions), which were, primary depolymerisation/condensation of the rubbers and (consecutive) degradation of the condensed product. They also reported a third devolatilisation reaction for SBR, which represented the devolatilisation of additives.

Han et al. (2018) applied the thermogravimetric analyser combined with a mass spectrometer to understand the waste tyre pyrolysis mechanism. They demonstrated that DTG curves of waste pyrolysis had a bimodal peak at 250-500°C and a small peak at 600-800°C. Moreover, the evolution of gas products detected by MS and the functional groups on the surface of the residue char identified by FTIR also proved that tyre pyrolysis could be divided into four stages. The first stage occurred below 320°C and was associated with minor mass loss due to water vaporisation and plasticiser decomposition. The second stage was attributed to the devolatilisation of NR at 320-400°C. The third stage took place at 400-520°C and relates to the devolatilisation of synthetic rubber, while an insignificant weight loss was observed at the fourth stage above 520°C. Recently, Gauthier-Maradei et al. (2019) presented a study focused on modelling a fixed bed reactor involving the determination of kinetic parameters to predict the tyre rubber (TR) pyrolysis through two steps. Firstly, the establishment of a reaction mechanism for degradation of TR based on the decomposition of its three main polymer compounds (NR, BR and SBR) using a differential scanning calorimetry (DSC). Subsequently, the kinetic parameters for each reaction were determined by the Borchardt-Daniels method using the heat flow obtained by DSC. In the second step, the authors included the chemical mechanism and the associated kinetic parameters in a developed mathematical model of a fixed bed reactor at a laboratory scale considering mass and energy balances. They proposed a general mechanism constituted by six reaction steps; three associated with primary pyrolysis (exothermic), two to secondary pyrolysis (endothermic) and one to a post-cracking reaction (exothermic, was observed for NR and SBR). Moreover, for the model proposed at 600°C, the scrap tyre rubber begins its thermal degradation after 11 min of reaction, obtaining a maximal liquid production at a reaction time of 18 min. The total consumption of the intermediate compounds occurs.

From the points discussed above, it can be deduced that there has been substantial literature data mainly focusing on the kinetic mechanism of tyre components devolatilisation. There seem to be agreements on the observations. However, little is known about product formation kinetics. Therefore, some recent research has been conducted to optimize pyrolysis process parameters and establish mathematical modelling to bring more insights into understanding the kinetic mechanism for the production of specific products.

For example, Ngxangxa (2016) developed both qualitative and quantitative gas chromatography-mass spectrometric (GC-MS) and comprehensive two-dimensional gas chromatography (GC×GC) methods for tyre derived oil (TDO) analysis of selected market-value compounds in TDOs. The abundant constituents present in the TDO were DL-limonene, p-cymene, benzothiazole, ethylbenzene, toluene, p-xylene, 3-ethyl toluene and α-terpinolene. N. M. Mkhize (2018), through a modification of the existing waste tyre pyrolysis processes, developed novel methods critical to maximising the DL-limonene yield in the pyrolysis oil with an improvement in the total TDO yield and quality [high quality characterised by high DL-limonene content and fewer heteroatom compounds (nitrogen-, oxygen- and sulphur-compounds, mainly benzothiazole)] observed. In another study, N. Mkhize et al. (2019) investigated the formation of isoprene and DL-limonene during WT pyrolysis in terms of the effect of heating rate (up to 100°C/min). They used a thermogravimetric analyser coupled with mass spectrometry (TGA/MS and reported that the peak temperature of both the isoprene and DL-limonene formation reactions increased with the increase in the heating rate. The latter is more significant than the one in isoprene. In addition, it was found that the maximum DL-limonene formation rate was relatively higher compared to maximum isoprene formation rate as the heating rate increased. Moreover, the model parameter estimation through the Kissinger method provided activation energies of approx. 133 and 115 $kJ.mol^{-1}$ for isoprene and DL-limonene formation reactions, respectively. Investigating the primary pyrolysis characteristics of WTs under different temperatures, Ding et al. (2015) adopted a setup based on an analytical pyrolyser coupled with gas chromatography/mass spectrometry (Py-GC/MS). They reported that the primary pyrolysis products of WT at 600°C were alkenes rather than alkanes or aromatics. Isoprene (18.7%) and D-limonene (22.9%) were found to represent the main compounds of chain alkenes and cyclic alkenes, respectively. The yield and selectivity of alkenes achieved the optimal at 600°C. To further understand the pyrolytic mechanism of WT, D-limonene was pyrolysed in Py-GC/MS to investigate the degradation procedure. It was indicated that, at low temperatures (≤ 500°C), the isomerisation reaction dominated the conversion process. When the temperature rose to 600°C and above, reactions such as internal cleavage of the C-C bond, intermolecular hydrogen transfer, and cyclisation to aromatics, were dominant. The bicyclic aromatics, such as indene and naphthalene, were also detected when the temperature was higher than 650°C. In addition, the TG-FTIR experiment exhibited that WT went through ring-opening and re-cyclisation reactions as the temperature exceeded a relatively high degree.

Menares et al. (2020) conducted a study of fast pyrolysis of WTs by quasi-isothermal thermogravimetric (TGA) analysis, kinetic modelling and analytical pyrolyser coupled with gas chromatography/mass spectrometry (Py-GC/MS). They reported that at up to 482°C, the WTs pyrolysis

is characterised by devolatilisation/condensation and depropagation reactions, while at higher temperatures, the cyclisation and aromatisation of primary products take place to form mostly monoaromatics. At temperatures below 500°C, isoprene (20.5%) and limonene (51%) were the major compounds detected (max. selectivity 71%) while at temperatures above 600°C, the formation of monoaromatics and gases was favoured with limonene and isoprene compositions being ruled by the equilibrated Diels-Alder reaction. Moreover, the kinetic parameters determined by model-based and isoconversional methods were in good agreement (101-176 kJ.mol^{-1}). In addition, proposing a simplified reaction map for WTs pyrolysis to explain the changes caused by the temperature in products composition, the authors concluded that the integration of TGA, Py-GC/MS and modelling allows understanding the reaction pathways controlling the WTs pyrolysis and, are the basis for estimating accurate kinetic parameters.

More recently, Q. Chen et al. (2022) investigated the thermal decomposition characteristics, reaction kinetics, high value-added products production and potential mechanisms during WT pyrolysis in the presence of Calcium Oxide using Thermogravimetry-Fourier Transform Infrared spectrometer (TG-FTIR) and Pyrolyser-Gas Chromatography/Mass Spectrometry (Py-GC/MS). They found that CaO accelerated depolymerisation terms of reducing the reaction temperature, with an effect on kinetic parameters. Additionally, the content of D-limonene increased by 13.76% and that of isoprene by 37.57%.

From the above, the kinetic mechanism studies on the thermochemical treatment of waste tyres mainly focused on tracking the devolatilisation of the main components of the tyre. A general mechanism can be observed from the literature and involves a first depolymerisation/condensation of the rubbers, a consecutive degradation of the condensed products and a third devolatilisation of additives. An insufficiency has been observed in works tracking the formation of valuable chemicals. From the limited data on the tracking of limonene and isoprene, it is broadly accepted that these two products are produced from NR, through a series of β-scission and depropagation reactions of polyisoprene and, by intramolecular cyclisation and scission of monomeric isoprene, respectively, with an equilibrium step of Diels-Alder reaction, Figure 2 (Menares et al., 2020; N. Mkhize et al., 2016).

The following sections discuss the most used methods and models for the solid-state kinetic mechanism study. A particular accent will be on the WTs pyrolysis mechanism study methods.

In a study to understand the influence of the variations in tyre composition on thermal degradation, Williams and Besler (1995) heated in a TGA, three different tyres (particle size < 1m and mass ~ 20 mg) at different heating rates (5, 20, 40 or 80 K/min) and compared the results with thermograms of three rubber compounds (NR, BR, and SBR). They found that areas of significant weight loss on the thermograms correspond to the weight loss patterns of one or more of the three rubbers and could derive kinetic parameters using the Arrhenius equation and its derived equations. Moreover, Williams and Besler's major initial pyrolysis products were isoprene, dipentene or other dimers. A further reaction resulted in the formation of a wide variety of compounds, directly by polymer chain scission or via degradation products of isoprene and dipentene, or via secondary reactions to form aromatic compounds. J. Conesa et al. (1997) studied the kinetics of the decomposition of tyre wastes when heating at different rates (1, 5 and 25˚C/min) during thermogravimetric measurements. They reported that the weight loss of WT in thermobalance can be as significant as 65% (35% solid residue) and that the weight loss takes place in three steps, the first corresponding probably to the decomposition of an oil fraction, the second to that of NR and the third to SBR. They proposed a model for the weight loss from which they concluded that the first fraction defined contributes with w_{10}=0.29 (45.17% of the total weight loss), the second fraction with w_{20}=0.23 (35.885% of the weight loss) and the third fraction with w_{30}=0.121 (18.95% of the total weight loss). Moreover, they

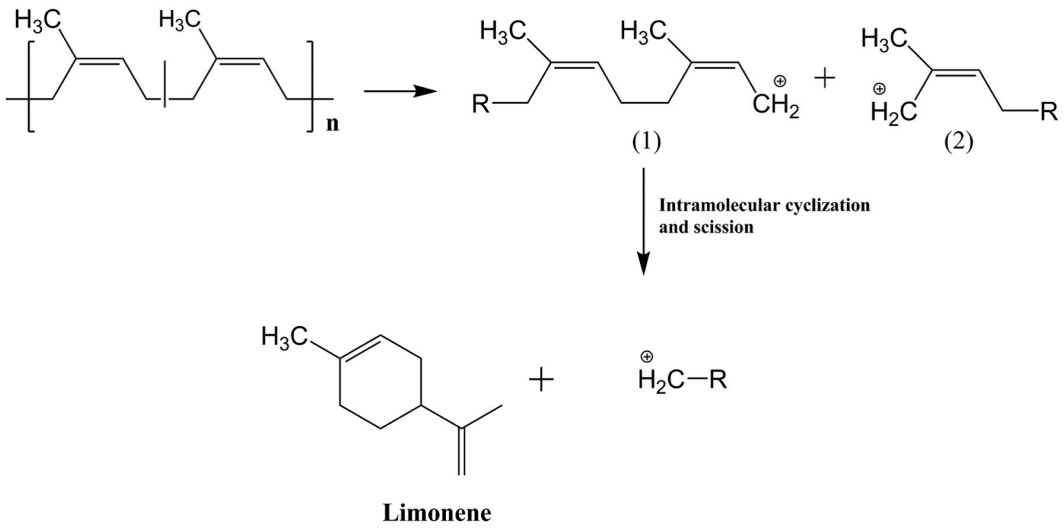

FIGURE 2: Limonene formation mechanism in tyre pyrolysis (G. Zhang et al., 2021).

observed that the first fraction that decomposes produces mainly CO_2 and linear hydrocarbons. CO_2 has also been formed in the second stage of decomposition (NR degradation), while SBR mainly produces aromatic compounds.

Quek and Balasubramanian (2009) developed a new model to provide insights into the pyrolysis kinetics of tyre by the use of an algorithm that includes two equations, one to count for heat conduction from the exterior to the interior of the tyre particle, and the other for mass transfer from within the tyre particle to the surface. They reported that the pyrolysis kinetics and the product composition and evolution are highly dependent on the heating rates maintained in the reactor. Specifically, at heating rates beyond 30 K/min, the TGA curves revealed an abrupt change in the pyrolysis process. However, the proposed model supposes that principal constituents of tyres are extender oil, NR, BR and SBR and that each of these components follows the basic Arrhenius-type equation with the first-order reaction. This model effectively described the influence of the various kinetic parameters on the pyrolysis reactions at different heating rates. Therefore, it is evident that incorporating heat and mass transfer processes in a pyrolytic model can improve the quantitative understanding of tyre pyrolysis, as was shown by the better fits of the model results at higher rates (>30 K/min). F.A. Lopez et al. (2013) determined the granulated scrap tyres (GST) thermal decomposition kinetics by TGA/DTG and compared the determined apparent activation energy and the pre-exponential factor values via the use of the Friedman, Flynn-Wall-Ozawa and Coats-Redfern model-free methods at different heating rates (5, 10, 15 and 20˚C/min). They showed that thermal decomposition starts at about 290˚C and is complete at 550˚C. The reaction begins with the dehydration and devolatilisation of the processing oils, followed by the NR and BR decomposition. The mean E_a values obtained by the different model-free methods used were similar, with an average of 160 kJ/mol and an average A of 2.49×10^{10} min^{-1}. However, as determined by the Coats-Redfern method, the thermal decomposition reaction model was accounted for by the D3 model. Moreover, the constant activation energy over the α interval (0.01-0.99) suggests that the pyrolysis of GST is a multi-step process.

Miranda et al. (2013) conducted a study of possible routes for the pyrolysis reaction mechanism of rubber tyre wastes (RT) in a micro-autoclave using an evaluation integrating both experimental data and different kinetic models. They evaluated kinetics models based on the results obtained at different temperatures (up to 350, 370, 390, 410, 430, 450˚C) and reaction times. They also established new reaction pathways involving a combination of series and parallel reactions in RT pyrolysis, as none of the mechanisms in the literature allowed the numerical adjustment to the experimental data. The authors proposed the reaction mechanisms based on: i) the physical state of the products obtained, ii) all reactions are elementary first-order and irreversible, iii) temperature dependence of the rate constants are described by the Arrhenius equation and, iv) there are no mass transfer resistances in the reaction medium.

Bart Danon and Görgens (2015) used a combined model-free and model-based kinetics employing a sophisticated devolatilisation mechanism to obtain the rubber composition of waste tyre crumbs. They predicted the rubber composition of three different WT crumbs using a kinetics model based on a sophisticated mechanism, including two consecutive devolatilisation reactions for the rubbers and a single intermediate condensed product. Using Friedman's method, the activation energies obtained were close for all the mixtures and in the range of 220 – 240 kJ/mol. These values were subsequently incorporated as fixed values in model-based kinetics, and pre-exponential factors were found to be strongly related to them, i.e., higher values of E result in higher values of A. the reaction order, however, remains around unity for lower values of E, while its value rises with higher values of E. The model was validated with binary and ternary mixtures of three predominant tyre rubbers (NR, BR and SBR) and subsequently applied for three WT crumbs consisting of different ratios of PCT and TT. The model was found capable of accurately predicting the natural polyisoprene content. B Danon et al. (2015) studied the devolatilisation behaviour of four rubbers (NR, PI, BR and SBR) by combined model-free (Friedman and Kissinger) and model-based kinetics and using a TGA-DTA instrument. They observed two distinct zones of weight loss for all four rubbers. These zones were the primary depolymerisation/condensation and the condensed product's secondary (subsequent) degradation. Moreover, data from DTG and DTA indicated that the two butadiene rubbers started to boil around 450˚C. The fixed values of the activation energy derived from the two isoconversional methods, ranging from 200 to 440 kJ/mol, were implemented as fixed values in a model-based kinetic procedure. The implementation resulted in a decrease in the degrees of freedom of the model-based multivariate nonlinear regression procedure. Therefore, the combined model-free and model-based approach was proved to accurately predict the devolatilisation of the four investigated rubbers.

3.2 Theoretical approaches

Throughout the modern history of thermal decomposition, the kinetic analysis of pyrolysis processes has gained justified interest from many investigators for two reasons (Uzun & Yaman, 2014): i) Kinetic data are crucial in designing any kind of device in which the thermal decomposition takes place, and ii) Kinetics is intrinsically related with the decomposition mechanisms. Kinetics is the starting point for postulating mechanisms for thermal decomposition.

Kinetic data from solid-state pyrolysis reactions have typically been obtained using discrete isothermal methods of analysis and is acquired by performing several experiments under isothermal conditions at different temperatures. Conversely, dynamic methods, which are performed under non-isothermal conditions, have attracted much appeal given their ability to investigate a range of temperatures expeditiously. Non-isothermal analytical techniques use modern thermobalances that subject samples to a programmed continuous temperature rise, ensuring that no temperature regions are omitted, as can occur during discrete isothermal measurements. In addition, studies have shown that there are wide disparities among values

obtained from dynamic techniques that use a single heating rate. A consensus emerged that the accuracy of these methods could be improved using multiple sets of thermal data collected by performing experiments at various heating rates (White et al., 2011).

Solid-state kinetics can be studied with thermal analytical methods by measuring a sample property as heated or held at a constant temperature. If a reaction involves weight loss, then the weight is followed throughout the reaction, and the kinetics are usually studied by thermogravimetric analysis (TGA). Heat, evolved or consumed, is another measurable property used for kinetic evaluation using differential scanning calorimetry (DSC) or differential thermal analysis (DTA). Weight loss or heat flow data are converted to a normalised form called conversion fraction (α). The conversion fraction ranges from 0 to 1 and measures reaction progress as a function of time or temperature (Khawam & Flanagan, 2006a).

3.2.1 Rate-laws

Equation 1 depicts the rate of a solid-state reaction in its most general form (Khawam & Flanagan, 2005):

$$\frac{d\alpha}{dt} = k(T)\, f(\alpha) \quad (1)$$

Where k is the reaction rate constant, f(α) is the reaction model, and α is the conversion fraction.

For isothermal thermogravimetric analysis, the conversion fraction at any time is (Khawam & Flanagan, 2006a):

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \quad (2)$$

Where: m_0 is the initial sample weight, m_t is the sample weight at time t, and m_∞ represents the final sample weight. Non-isothermal, the conversion fraction at any temperature is:

$$\alpha = \frac{m_0 - m_T}{m_0 - m_\infty} \quad (3)$$

Where: m_t is the sample weight at temperature T

Integrating the above equation gives the integral rate law,

$$g(\alpha) = kt \quad (4)$$

Where: g(t) is the integral degradation model.

The temperature dependence of the rate constant is described by the following Arrhenius equation,

$$k = Ae^{-E_a/RT)} \quad (5)$$

Where: A is the pre-exponential (frequency) factor, E_a is the activation energy, T is the absolute temperature, and R is the gas constant.

Substituting Equation 5 in the above rate expressions gives,

$$\frac{d\alpha}{dt} = Ae^{-E_a/RT}\, f(\alpha) \quad (6)$$

And,

$$g(\alpha) = Ae^{-E_a/RT}\, t \quad (7)$$

Equation 6 and 7 can be transformed into non-isothermal rate expressions describing reaction rates as a function of temperature and at a constant heating rate by utilising the following equation,

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt}\,\frac{dt}{dT} \quad (8)$$

Where: dα/dT is the non-isothermal reaction rate, dα/dt is the isothermal reaction rate, and dT/dt is the heating rate (β).

Substituting Equation 6 in the above equation gives the differential form of the non-isothermal rate law,

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E_a/RT} f(\alpha) \quad (9)$$

Upon integration, Equation 9 gives,

$$g(\alpha) = \frac{A}{\beta} \int_0^T e^{-E_a/RT}\, dT$$

If Ea/RT is replaced by "x", and the integration limits are transformed; the above equation becomes,

$$g(\alpha) = \frac{AE_a}{\beta R} \int_x^\infty \frac{e^{-x}}{x^2}\, dx \quad (10)$$

Which is written as,

$$g(\alpha) = \frac{AE_a}{\beta R}\, p(x) \quad (11)$$

Where p(x) is the exponential integral.

The exponential integral p(x) has no analytical solution but has many approximations. Thus, the approximation of temperature integral is the key to understanding the different analysis methods (Starink, 2003). The main approaches used for evaluating the temperature/exponential integral are (Khawam & Flanagan, 2006a): i) calculating values of p(x) numerically, ii) converting p(x) to an approximate form that can be integrated and, iii) approximating p(x) by a series expansion. There are three approximations that have been used frequently over the years (Flynn, 1997; Flynn & Wall, 1966): Schlömilch Expansion, Asymptotic expansion and Expansion in a series of Bernoulli Numbers.

Thus, these asymptotic expansions are generally expressed in the form (Starink, 2003):

$$p(x) = \frac{e^{-x}}{x(w+x)}(1 + g(x)) \quad (12)$$

Where: w is a constant, g(y) is an expansion of which the first term is of the order y^{-1} or y^{-2}, with g(y)"1, providing y is more significant than about 10. By taking non-integer values of w, many more expansions can be derived. One of them is the approximation made by Senum and Yang described by the equation,

$$p(x) \cong \frac{e^{-x}}{x^2} h(x) \quad (13)$$

With h(x) is the ratio of two polynomials, its fourth-order approximation is given by,

$$h(x) = \frac{x^4 + 18x^3 + 86x^2 + 96y}{x^4 + 20x^3 + 120x^2 + 240y + 120} \quad (14)$$

This expansion is generally limited to only the first term or the first two terms for deriving p(x). Equation 15 gave the first term expansion and led to the Kissinger-Akira-Sunose method (Starink, 2003).

$$p(x) \cong \frac{e^{-x}}{x^2} \quad (15)$$

The two first terms approximation has been used by Coats and Redfern and is given by:

$$p(x) \cong \frac{e^{-x}}{x^2}\left(1 - \frac{2}{x}\right) \quad (16)$$

Doyle, however, suggested a linear approximation of the logarithm of p.

$$\log p(x) \cong -0.4567x - 2.315 \quad (17)$$

The determination of the function f(α) and the constants A and E are required for a complete description of the reaction progress at all temperatures and for all temperature-time programmes.

3.2.2 Models and mechanisms

A model is a theoretical and/or mathematical description of what is observed experimentally. In solid-state reactions, a model describes a reaction and can usually be converted into a mathematical expression, i.e., rate expression (Khawam & Flanagan, 2006a). Models are generally categorised based on the graphical shape of their isothermal curves (α vs t or dα/dt vs α) or their mechanistic assumptions. Based on their profile, kinetic models can be grouped into acceleratory, decelerator, linear, or sigmoidal models. Based on mechanistic assumptions, models are classified into nucleation, geometrical contraction, diffusion, or reaction-order (Table 2) (Khawam & Flanagan, 2006b). However, Šesták and Berggren (1971) have suggested a mathematical form that represents all models in a single general expression:

$$f(\alpha) = \alpha^m (1-\alpha)^n (-\ln(1-\alpha))^p \quad (18)$$

With m, n, and p, the constant factors

By assigning values to the three variables, any model can be expressed. The above equation has been simplified by Perez-Maqueda et al. (2006) into a simple form and was found able to describe every kinetic model just by selecting the proper c, n and m parameters:

$$f(\alpha) = c(1-\alpha)^n \alpha^m \quad (19)$$

An alternative method for determining a plausible kinetic model can be based on a modified master plot, comparing the theoretical curves with the experimental ones. The master plot is a characteristic curve independent of the measurement condition, easily obtained from experimental data and based on both the first and the second derivatives of α (Criado et al., 1989). The master plots are referenced theoretical curves depending on the kinetic model but generally independent of the kinetic parameters. As in many cases, the experimental kinetic data can easily be transformed to the experimental master plots, comparison of the theoretical master plots drawn by assuming various kinetic models with the experimental master plot allows the selection of the appropriate kinetic model of the process under investigation or, at least, of the type of proper kinetic models. This method can be applied to the kinetic analysis of solid-state reactions, whatever the type of temperature program used for recording data. A single curve is enough to construct the experimental master plots in isothermal conditions. In non-isothermal states, the knowledge of both α as a function of temperature and activation energy is required to calculate the master plot curves from the experimental data (Gotor et al., 2000).

Today, a significant step in the pyrolysis process is intensifying the use of pyrolysis reactors, for which a kinetic model must be appropriately maintained to fully describe the complexity of the processes that occur during the thermal degradation of large polymer chains (Khiari et al., 2018). A general objective of modelling thermally activated reactions is to derive a complete description of the progress of a valid reaction for any thermal treatment, be it isothermal, by linear heating or any other non-isothermal treatment (Starink, 2003).

In solid-state kinetics, mechanistic interpretations usually imply identifying a reasonable reaction model because information about individual reaction steps is often challenging to obtain. However, the choice of a reaction model requires other complementary techniques such as microscopy, spectroscopy, X-ray diffraction, etc. (Khawam & Flanagan, 2006b). Thus, the modelling of tyre pyrolysis kinetics gives an overview of the mechanisms responsible for the decomposition process and predicts the potential difficulties in the pyrolysis reactor (Khiari et al., 2018).

3.2.3 Methods for WT kinetic study

Several methods used to study solid-state kinetics are also utilised for WT pyrolysis kinetics. These methods can be generally grouped into experimental and computational categories (Khawam & Flanagan, 2006a).

Experimental methods

Isothermal and non-isothermal methods are utilised to obtain solid-state kinetic data. Isothermal methods are based on maintaining samples at several constant temperatures, and as a result, a set of α – time points are produced at each temperature. These methods are based on the isothermal rate equations (Equation 6 and 7). Non-isothermal or dynamic methods involve heating samples at constant heating rates (usually linear) and following the reaction course (Khawam & Flanagan, 2006a).

The determination of kinetic parameters by non-isothermal methods present some advantages such as i) the kinetics can be established over an entire temperature range continuously, ii) the possibility to obtain a lot of information such as temperature at maximum devolatilisation rate, characteristic temperatures, and kinetic parameters with a single sample, iii) avoidance of sample-to-sample error by using a single sample, and iv) avoid some degradation that may occur during the preheating period, mainly when the temperature of onset of reaction is considerably lower than the temperature of isothermal trials (Carrasco, 1993).

Calculation methods

Two groups of methods are used to analyse either isothermal or non-isothermal solid-state kinetic data, model-fitting and model-free methods (Khawam & Flanagan, 2006a). Several researchers have regrouped these methods into several classes depending on their derivation basis. For example, Flynn and Wall (1966) classified the different methods of kinetic analysis into five categories, i.e., integral methods utilising weight loss versus temperature data directly, differential methods using the rate of weight loss, difference-differential methods involving differences in rate, methods especially applicable to initial rates and, nonlinear or cyclic rate methods. In the same way, Carras-

TABLE 2: Solid-state rate expressions for different reaction models (Khawam and Flanagan, 2006b).

Model	Differential form $f(\alpha)=1/k\ d\alpha/dt$	Integral form $g(\alpha)=kt$
Nucleation models		
Power law (P2)	$2\alpha^{1/2}$	$\alpha^{1/2}$
Power law (P3)	$3\alpha^{2/3}$	$\alpha^{1/3}$
Power law (P4)	$4\alpha^{3/4}$	$\alpha^{1/4}$
Avrami – Erofeyev (A2)	$2(1-\alpha)\ [-ln(1-\alpha)]^{1/2}$	$[-ln(1-\alpha)]^{1/2}$
Avrami – Erofeyev (A3)	$3(1-\alpha)\ [-ln(1-\alpha)]^{2/3}$	$[-ln(1-\alpha)]^{1/3}$
Avrami – Erofeyev (A4)	$4(1-\alpha)\ [-ln(1-\alpha)]^{3/4}$	$[-ln(1-\alpha)]^{1/4}$
Prout – Tompkins (B1)	$\alpha(1-\alpha)$	$ln[\alpha/(1-\alpha)]$
Geometrical contraction models		
Contracting area (R2)	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
Contracting area (R3)	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
Diffusion models		
1-D diffusion (D1)	$1/(2\alpha)$	α^2
2-D diffusion (D2)	$-[1/ln(1-\alpha)]$	$(1-\alpha)ln(1-\alpha)+\alpha$
3-D diffusion – Jander (D3)	$[3(1-\alpha)^{2/3}]/[2(1-(1-\alpha)^{1/3}]$	$(1-(1-\alpha)^{1/3})^2$
Ginstling – Brounshtein (D4)	$3/[2((1-\alpha)^{-1/3}-1)]$	$1-(2/3)\alpha-(1-\alpha)^{2/3}$
Reaction-order models		
Zero-order (F0/R1)	1	α
First-order (F1)	$(1-\alpha)$	$-ln(1-\alpha)$
Second-order (F2)	$(1-\alpha)^2$	$[1/(1-\alpha)]-1$
Third-order (F3)	$(1-\alpha)^3$	$(1/2)[(1-\alpha)^{-2}-1]$

co (1993) classified the methods into integral, differential and special methods. They defined special methods as those that cannot be classified as integral or differential. They are generally based on detailed experimental data or need data previously evaluated from graphical plots. However, Ortega (2002)1) stated three methods used to overcome different limitations found in fitting kinetics data: i) the empirical function which is the equation of Sestak and Beerggren, ii) the master plots and, iii) the isoconversional methods.

In a non-isothermal experiment, both T and α vary simultaneously. The model-fitting approach generally fails to achieve a clean separation between the temperature dependence k(T), and the reaction model, f(α). As a result, almost any f(α) can satisfactorily fit data at the cost of drastic variations in the Arrhenius parameters. In addition, because isothermal and non-isothermal experiments are conducted in different temperature regions, if decomposition involves several steps with varying energies of activation, the contributions of these steps to the overall decomposition rate measured in the thermal analysis experiment will vary with both temperature and extent of conversion. This means that the effective activation energy determined from thermal analysis experiments will also be a function of these two variables. The usual implementation of model-fitting methods aims to extract a single value of the activation energy for an overall process. Therefore, the value obtained in such a way is an average and does not reflect changes in the reaction mechanism and kinetics as a function of temperature and the extent of conversion (Vyazovkin & Wight, 1999).

The drawbacks mentioned above of model-fitting can be avoided with the use of isoconversional methods. Firstly, these methods allow the determination of the activation energy as a function of the extent of conversion and/or temperature. Secondly, this dependence is determined without making any assumptions about the reaction model. Hence, these methods are likely to produce consistent kinetic results from isothermal and non-isothermal experiments.

Therefore, the model-free isoconversional methods emerge as an alternative to model-fitting methods for their attractive attributes that i) they can be used to analyse either isothermal or non-isothermal data, ii) results from isothermal and non-isothermal experiments are internally consistent, and iii) the explicit evaluation of E_a - α dependencies can reveal complexities in the reaction kinetics (Vyazovkin & Wight, 1999).

Table 3 (*please see the supplementary material)* presents the commonly used methods in the Kinetics study of WT pyrolysis with their characteristic equations.

It is worth noting that:

- The Coats-Redfern Method model gives entirely satisfactory results when kinetics follow a simple order(-Flynn & Wall, 1966) but presents no significant difference, at low conversion levels, between zero and first-order kinetics (Carrasco, 1993).
- The Freeman-Carroll Difference-Differential method shows some imprecisions because both the first and

the second conversion derivatives are calculated from differences between two discrete experimental points (Δf/ΔT). Moreover, due to the approximation $\frac{d^2f}{dT^2} \approx \frac{\Delta^2 f}{\Delta T^2}$, this method is, therefore, of low accuracy (Flynn & Wall, 1966).

- Friedman's method applies to data sets obtained at different heating rates β_i and/or different temperatures T_i (Venkatesh et al., 2013). However, it requires numerical differentiation of the experimental α versus T curves that typically results in quite noisy rate data and thus, unstable E_a values. This drawback is avoided by using integral isoconversional methods (Vyazovkin & Sbirrazzuoli, 2006).
- The Kissinger Method, compared to the isoconversional methods, the Kissinger method has a limitation because it produces a single value of the activation energy for the whole process. As a result, the obtained value is sound only if there is no variation of E_a with α throughout the process. Unfortunately, such variations are pretty typical, and the Kissinger method cannot detect them. Therefore, the E_a values obtained by this method should generally be treated with caution unless an isoconversional approach has demonstrated E_a to be independent of α (Vyazovkin & Sbirrazzuoli, 2006).
- Starink's method integrates the isoconversional approaches of Flynn-Wall-Ozawa and Kissinger-Akira-Sunose into a single expression. This method, applied in several kinetic studies, appears to be at least an order of magnitude more accurate than the two FWO and KAS approaches (Starink, 1996, 2003).

4. GAP IN KNOWLEDGE

The present study provides a comprehensive overview of the current knowledge regarding the pyrolysis of waste ground tyre rubber and discuss the waste ground tyre rubber kinetics mechanisms and modelling approaches, there are several areas that present gaps and require further investigation.

- Lack of consensus on parameter relationships: the study highlights the lack of agreement among different studies on the relationship between product yields and various parameters. This indicates a need for more systematic and standardized research to establish clear correlations between the operating conditions and the resulting product composition. Further investigation is necessary to determine the optimal conditions for different types of feedstock and to understand the interactions between various pyrolysis parameters.
- Limited understanding of reaction pathways: the study acknowledges that the kinetic mechanism studies on waste ground tyre rubber pyrolysis are inadequate. While there has been some focus on tracing the devolatilisation of main components, there is little of research on the formation of specific chemicals and their kinetics. Investigating the formation of important chemicals during pyrolysis, such as limonene, terpinolene, indene or p-cymene, would provide valuable insights into the reaction pathways and help optimize the process for desired products outcomes.
- Lack of scalability and economic viability assessment: while the study provides a theoretical understanding of the kinetic mechanisms underlying waste ground tyre rubber pyrolysis, there is a lack of discussion on the scalability and economic viability of the process. Assessing the feasibility of large-scale implementation, including cost analysis, energy requirements, and environmental impacts, is crucial for evaluating the practical applicability of pyrolysis as a waste management solution. Future research should focus on bridging the gap between laboratory-scale studies and real-world implementation.
- Integration of experimental and modelling approaches: the study briefly mentions the integration of the thermogravimetric analysis (TGA), pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS), and modelling as a promising approach to understanding reaction pathways. However, there is a need for more comprehensive studies that combine experimental data with rigorous kinetic modelling techniques. Such integration would enable accurate predictions of product yields and composition under different operating conditions and aid in the optimization of the pyrolysis process.

5. CONCLUSIONS AND FUTURE PERSPECTIVE

This paper reviewed the progress in understanding mechanisms underlying the WGTR pyrolysis process. Based on various data from the literature, the WGTR pyrolysis is dependent on its operating parameters, primarily the temperature. The review included a comprehensive discussion of the effects of various parameters on product yields and properties. Several authors have initiated kinetics studies to understand the reactions pathways to design the process reactors better and increase the process's economic viability. The study presented and discussed solid-state kinetics models and methods for determining kinetic parameters. The literature has revealed that selecting the correct form of the model function and choosing the proper determination method would result in a more accurate prediction of WGTR pyrolysis mechanisms. Due to the average values of kinetic parameters obtained (E_a ranging from 101-176 $kJ.mol^{-1}$), model-fitting approaches cannot disclose the complexity of reactions in solid-state thermos analysis. The model-free isoconversional methods, on the other hand, allow unmistakably detecting multi-step kinetics dependence of the activation energy on the extent of conversion. Still, they are also subject to some uncertainties, owing to the approximations necessary for their applicability. As a result, a trend has arisen to combine the two approaches to predict mechanisms better.

Furthermore, recent studies have shown that the integration of TGA, Py-GC/MS and modelling allows for a deeper understanding of the reaction pathways that regulate WGTRs pyrolysis, laying the groundwork for future research in this field. From the literature, the thermal devol-

atilisation of the WGTRs can be characterised by devolatilisation/condensation reactions with subsequent conversion of radicals, monomers and dimers to char, volatiles and gas. Moreover, depending on the temperatures and bond energies, the process balances endothermic and exothermic reactions. The studies have shown a maximum yield of limonene and isoprene of 51% and 20.5% respectively, at temperature around 500°C. The isoprene yield has been found to increase more to up to 37.57% with the use of catalyst such as CaO.

However, the kinetic mechanism studies on the thermochemical treatment of waste tyres are inadequate and restricted due to an emphasis on profiling/tracking devolatilisation of the feedstock's main components rather than tracking the chemicals' formation such as limonene, terpinolene, indene and p-cymene. The limited information available in the literature focuses primarily on increasing DL-limonene in TDO and estimating kinetic parameters related to the formation of isoprene and DL-limonene. As a result, further research is needed to correlate the yields of significant chemicals to kinetic data and reach general agreements on the reaction pathways, thereby increasing the process's economic viability. Moreover, since the reaction routes for WGTRs pyrolysis are sensitive to the material composition, particle sizes, thermal regime (heat or kinetic control) and, thus, to the experimental system, more research into the influence of these parameters on the kinetics and selectivity to attractive fractions or chemicals will aid process design and scaling up.

WGTR pyrolysis has undergone significant industrial development in recent years, evolving from a promising concept to a mature and economically viable waste management solution. This industrial growth has been driven by a combination of environmental imperative, economic incentives, and technological advancements. The economic viability of industrial WGTR pyrolysis is a primary concern, with companies conducting feasibility studies to assess factors like feedstock availability, product marketability, and return on investment. Hence, the are ongoing research and development efforts dedicated to improving process efficiency, developing novel catalysts, and exploring innovative applications for pyrolysis products.

While the study provides valuable insights into the kinetic mechanisms underlying waste ground tyre rubber pyrolysis, there are several areas that require further investigation. Future research should focus on establishing clear correlations between operating parameters and product yields, understanding the formation of specific chemicals during pyrolysis, characterizing pyrolysis products in greater detail, assessing the scalability and economic viability of the process, and integrating experimental and modelling approaches. Addressing these gaps will contribute to the development of more efficient and sustainable waste management strategies for waste ground tyre rubber.

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HYDROTHERMAL CARBONIZATION OF SEWAGE SLUDGE – AN EFFECTIVE APPROACH TO TREAT AND MANAGE SEWAGE SLUDGE IN RURAL AREAS OF GERMANY?

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ABSTRACT

As the result of new regulation from the German Sewage Sludge Ordinance (AbfKlärV 2017) and the future obligation to recover phosphorus, thermal treatment (mono-incineration) has become increasingly popular, whereas land-based utilization has decreased. Germany has produced 1.71 million metric tons (dry matter) of sewage sludge in the year 2021. Sewage sludge contains important nutrients such as phosphorus but also heavy metals and organic pollutants making the direct utilization of sewage sludge in agriculture controversial. Rural areas in particular have benefited from land-based sewage sludge utilization however the future ban on direct land-based utilization is forcing them to find alternative solutions for sewage sludge treatment and management. Hydrothermal carbonization (HTC) has developed considerably over the last 15 years and offers a viable alternative for the utilization of municipal and industrial organic waste such as sewage sludge. The process takes place in an aqueous environment without the need for pre-drying sewage sludge and thereby facilitating direct processing. HTC is especially suitable in combination with the recovery of nutrients like phosphorus. Technologies to recover this essential resource are important because phosphorus is an element that cannot be substituted and is therefore essential. HTC could make a significant contribution to sewage sludge management in combination with phosphorus recovery. However, the technology has yet to establish itself as a sewage sludge valorization process (2023) and is not yet a recognized state-of-the-art. Nevertheless, the HTC technology could gain greater relevance in the future, especially as an alternative valorization pathway for sewage sludge in rural areas of Germany.

1. INTRODUCTION

Sewage sludge is the waste generated from the treatment of wastewater in wastewater treatment plants (WWTP). The sludge is a by-product in addition to the treated wastewater which contains nutrients and has to be utilized (Huezo et al., 2021). Sewage sludge can be divided into primary, secondary and tertiary sludge (Roskosch et al., 2018). Primary sludge is also known as pre-sludge, is produced through sedimentation in primary clarifiers during the mechanical-physical treatment of effluent. Secondary sludge is divided into return sludge and activated sludge. Secondary sludge is separated from treated wastewater in secondary clarifiers. The sludge produced during further wastewater treatment is called tertiary sludge. For instance, phosphate elimination processes used in downstream chemical purification produce this (Roskosch et al., 2018). The term raw sludge refers to non-stabilized or partially stabilized sludge (AbfKlärV, 2017).

The Federal Statistical Office of Germany indicates that 1,717,803 t DM (dry matter) of sewage sludge was generated in the year 2021 (Destatis, 2023). The current trend of sewage sludge utilization is greatly shifting towards thermal utilization and no longer towards land-based utilization. In addition to nutrients, sewage sludge also contains heavy metals and organic pollutants making its direct application for agriculture purposes difficult (Aragón-Briceño et al., 2021). In Germany, sewage sludge disposal options have become progressively limited as a result of advanced environmental policies and the laws that have been adopted over the last decade. According to the German Sewage Sludge Ordinance (AbfKlärV 2017), sewage treatment facilities larger than 100,000 population equivalent (PE) and 50,000 population equiv-

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alents (PE) will no longer be allowed to recycle sewage sludge for land-based utilization starting in 2029 and 2032, respectively. About 79% of the total amount of sewage sludge generated in 2021 (1,364,890 t DM) in Germany was thermally utilized (including mono- and co-incineration among other thermal disposals) and the amount of sewage sludge managed through land-based use and landscaping is gradually declining. Figure 1 shows the trend in sewage sludge utilization in Germany from 2015-2021 (Destatis, 2023).

The sewage sludge producers are required by the German Sewage Sludge Ordinance to recover phosphorus from the sludge on a mandatory basis. Phosphorus recovery from the ash or carbonaceous residue is done after the mono-incineration of sewage sludge. Alternatively, the co-incineration of sewage sludge can be done only after reducing the phosphorus content to at least 50% or to < 20 g P/kg DM. The sewage sludge that resulted could only be used thermally in co-incineration (e.g., cement plant, power plant, waste incineration) after meeting this requirement (AbfKlärV 2017; Mix-Spagl, 2017). All sewage sludge producers are required to voluntarily inform the relevant authority by 31st December 2023 of their future plans for recovering phosphorus. An obligation to recover phosphorus will come into existence in the year 2029 for all WWTP that treat municipal wastewater (Montag et al., 2022). Another considerable regulation in the context of land-based utilization is the German Fertiliser Ordinance (DüMV 2012). Among the other regulations, this ordinance regulates the placing on the market of fertilizers that are not designated as EG-fertilizers (Roskosch et al., 2018). Furthermore, this regulation classifies sewage sludge as an organic or organic-mineral fertilizer and makes a provision to be used as fertilizer if it meets the specified limits (Roskosch et al., 2018). In addition to the limit values in the Sewage Sludge Ordinance (AbfKlärV 2017), those in the Annex to the German Fertiliser Ordinance (DüMV 2012) also apply to the agricultural-based utilization of sewage sludge. As a result, the possibilities for direct land-based utilization are limited especially in the case of heavy metals.

The typical composition of sewage sludge is shown in Table 1. Table 1 also depicts the limit values of the German Fertilizer Ordinance (DüMV 2012) and German Sewage Sludge Ordinance (AbfKlärV 2017) for direct land-based applications. If sewage sludge does not comply with the qualitative requirements of the German Fertilizer Ordinance and German Sewage Sludge Ordinance, it has to be recycled in other ways (Langenohl, 2015).

Stringent regulations from the German Sewage Sludge Ordinance, (AbfKlärV 2017) and the future obligation of phosphorus recovery has made thermal valorization increasingly popular whereas land-based utilization and landscaping have decreased. Rural areas in particular have benefited from land-based sewage sludge utilization.

As previously stated, land-based application of sewage sludge was the most common method for managing and utilizing sewage sludge in rural areas. Since this recycling method is about to be phased out, there is growing interest in finding alternative ways to recycle sewage sludge and recover phosphorus. In this concern, thermal valorization (mono-incineration) of sewage sludge in combination with phosphorus recovery from ash might be widely accepted. The primary requirement of sludge to be dewatered and dried however makes the incineration process cost-intensive and poses concerns related to the release of toxic air pollutants (NO_x, SO_2, and dioxins) if the incineration process is not managed properly (Shettigondahalli et al., 2022). Small and medium-sized WWTPs and municipalities will need to find alternative methods of sewage sludge management and treatment in the future if they do not have access to such thermal sludge valorization opportunities.

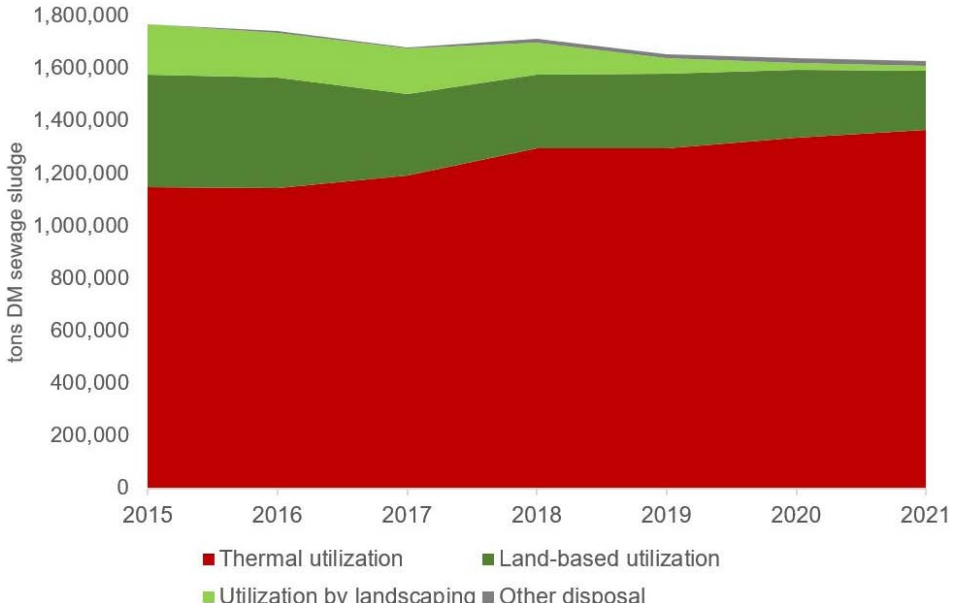

FIGURE 1: Development of the sewage sludge utilization in Germany 2015-2021 - data based on (DESTATIS, 2023).

TABLE 1: Composition of digested and dewatered sewage sludge according to Basse et al., 2012 and Roskosch et al., 2018.

Paramter	Unit	Range for sewage sludge	Limit values according to DüMV 2012 or AbfKlärV 2017 [mg/kg DM]
Water	Wt.-% (raw)	65 - 75	
Ash	Wt.-% (wf)	30 - 50	
LHV	MJ/Kg (raw)	1 - 2 / 10 - 12	
C	Wt.-% (wf)	33 - 50	
H	Wt.-% (wf)	3 - 4	
O	Wt.-% (wf)	10 - 20	
N	Wt.-% (wf)	2 - 6	
S	Wt.-% (wf)	0.5 - 1.5	
Fl	Wt.-% (raw)	aprox. 0.01	
Cl	Wt.-% (raw)	0.05 - 0.5	
P	g/kg (raw)	2 - 55	
Sb	mg/kg (raw)	5 - 30	
As	mg/kg (raw)	4 - 30	40
Pb	mg/kg (raw)	70 - 300	150
Cd	mg/kg (raw)	1.5 – 4.5	1.5
Cr	mg/kg (raw)	50 - 80	
Cu	mg/kg (raw)	300 - 350	
Mn	mg/kg (raw)	600 - 1,500	
Ni	mg/kg (raw)	30 - 35	80
Se	mg/kg (raw)	1 - 5	
Tl	mg/kg (raw)	0.2 - 0.5	1
V	mg/kg (raw)	10 - 100	
Hg	mg/kg (raw)	0.3 - 2.5	1
Zn	mg/kg (raw)	100 - 300	4,000
Sn	mg/kg (raw)	30 - 80	
AOX	mg/kg DM	200 - 400	400
PCB6	mg/kg DM	0.01 - 0.02	0.1
PCDD/dl-PCB	mg/kg DM	0.000005 – 0.0001	0.00003

2. HYDROTHERMAL CARBONIZATION OF SEWAGE SLUDGE

2.1 Operating conditions and reaction pathway

Hydrothermal carbonization (HTC) is a promising alternative for the management of sewage sludge and the process used moist waste as a reaction medium to convert biomasses into a lignite-like hydrochar. In contrast, other thermo-chemical conversion processes such as incineration and pyrolysis, are not suitable particularly for moist municipal and industrial organic waste like sewage sludge as it requires pre-drying (Wang et al., 2019B). A major advantage of the HTC technology is the possibility of processing the sewage sludge directly without further drying. As a result, the mechanically dewatered sewage sludge generated at WWTP could be processed directly (Wang et al., 2020). HTC has gained increasing interest from the research community and there are many scientific studies dealing with the hydrothermal treatment of sewage sludge like digested sludge (Huzeo et al., 2021), and raw sludge (Blach and Engelhart, 2020) or primary sludge (Danso-Boateng et al., 2015).

HTC converts sewage sludge into a carbonaceous product (hydrochar) while simultaneously recovering phosphorus from it by utilizing moisture present in sewage sludge as a catalyst, reactant, and solvent (Kruse et al., 2013). The sewage sludge is converted to a carbonaceous product under temperatures (180°C-280°C) and pressures below the saturation vapor pressure in several parallel or serial chemical reaction mechanisms (Reza et al., 2014a). During the process a series of reactions results in numerous dissolved intermediates. Polymers like carbohydrates first break down into simpler components (e.g., di- and monosaccharides) by hydrolysis. The hydrolysis of cellulose produces glucose and fructose. Lignin, on the other hand, is converted to phenol (Kruse et al., 2013). As the HTC process continues, various platform chemicals such as 5-HMF (5-(Hydroxymethyl)-2-furaldehyde), furfural, or levulinic acid are formed. Furthermore, Maillard reactions take place at certain reaction temperatures and reaction times, which contributes to the formation of hydrochar but also leads to high contents of total organic carbon (TOC) and total nitrogen (TN) in the resulting HTC process water (Xu et al., 2022; Djandja et al., 2021). The decisive reaction that leads to the formation of hydrochar is aldol condensation (Shi et al., 2019). The resulting hydrochar from HTC of sewage sludge is essentially hygienic, easy to dewater, free of pharmaceuticals, and expected to exhibit moderate energy density (Crocker et al., 2011; Saetea and Tippayawong, 2013). The yield of hydrochar produced depends on various reaction parameters, of which temperature and reaction time play a decisive role (Huezo et al., 2021; Djandja et al., 2021; Blach and Engelhart, 2020).

2.2 Fate and behavior of heavy metals and organic pollutants during HTC

As described in the introduction section, sewage sludge contains heavy metals along with organic pollutants. They are omnipresent in the environment and end up in sewage sludge from households and industries, among others (Roskosch et al., 2018). The sludge absorbs the heavy metals by passive sorption and active uptake through the accumulation of living cells (Geng et al., 2020).

Hydrothermal carbonization of sewage sludge has effects on the distribution of heavy metals. Wang et al., 2019A concluded that the heavy metal distribution depends on the reaction severity and suspected immobilization into the hydrochar. Wang et al, 2020 confirmed the assumption of redistribution of heavy metals in the liquid and solid phases. In particular, the metals Al, Fe, Zn, and Mn are immobilized in the char during the process under neutral conditions. Less than 5% of the heavy metals were detected in the resulting process water. However, acidic conditions result in a weaker enrichment of heavy metals into the solid phase. The immobilization depends mainly on the reaction temperature and reaction time (Wang et al., 2020). Furthermore, due to the immobilization of the heavy metals, the ecotoxicity is low (Liu et al., 2018; Wang

et al., 2020). In addition to heavy metals, the fate of organic contaminants in sewage sludge, such as drug residues, is important. Vom Eyser et al., 2015, studied the removal of twelve pharmaceuticals (including ibuprofen and erythromycin) in sewage sludge during HTC. Seven of the pharmaceutical substances were either or the proportion in the hydrochar was reduced (39% to ≥ 97%) (vom Eyser et al., 2015). The heavy metals and organic impurities in the hydrochar from sewage sludge turn its suitability as fertilizer into a critical issue. However, vom Eyser et al., 2015 only investigated the fate of the pharmaceuticals in the respective hydrochar and not in the process water (PW). The PW can contain organic pollutants like phenols, aromatic compounds, alkenes, and pyrazines (Usman et al., 2019).

2.3 Process water as a by-product

The solid-liquid separation after hydrothermal carbonization of the sewage sludge produces two phases. On one side is the hydrochar and on the other side is the process water (PW). The PW is inorganically and organically polluted and has to be treated. Quicker and Weber, 2016 give ranges of values for COD from 4,900.00 - 78,000.00 mg l^{-1}, for BOD_5 1,700.00 - 42,000.00 mg l^{-1} and TOC 4,000.00 - 31,700.00 mg l^{-1}. If left untreated, it would be a burden on water bodies and thus on the environment (Leng et al., 2021). Particularly, the formation of persistent and toxic organic compounds during HTC that can leach into the PW remains a challenge. These substances are occasionally difficult to degrade biologically and may complicate the PW treatment. The composition of the PW depends primarily on the waste biomass used at the beginning and the reaction parameters (Woriescheck, 2019; Usman et al., 2019). Chen et al., 2019 found that PW from HTC of dewatered sewage sludge contains mainly proteins and short-chain fatty acids, but also poorly degradable compounds such as humic acids, melanoidins, nitrogen heterocycles, and phenols. A major challenge of PW management besides the actual contamination of the PW is the large quantities that would be produced during the industrial, continuous process of an HTC plant. Additionally, the legal requirements for PW treatment can also pose additional challenges. HTC-PW in Germany is categorized as wastewater and has to be treated and disposed of as such (§ 56 German Federal Water Act, WHG). This is done either to a direct discharge quality which allows direct discharge into the environment (§ 57 WHG) or to an indirect discharge quality which allows discharge and subsequent treatment in a municipal WWTP (§ 58 WHG). Respective requirements and limit values must be met for both alternatives.

The minimum requirement values for the discharge of wastewater into a water body or municipal WWTP are described in the German Waste Water Ordinance (AbwV) and the associated annexes. The treatment must be carried out according to the state of the art. For process waters from hydrothermal treatment, the requirements of Annex 27 "Treatment of waste by chemical and physical processes (CP plants) and waste oil regeneration" apply (AbwV 1997).

There is currently no continuous industrial implementation of HTC technology that includes process water management and treatment. One opportunity to manage the large quantities of PW is to reuse it as a partial flow in the HTC process and therefore save fresh water (if needed) and reduce the costs associated with it (Kambo et al., 2018). This step should be chosen to reduce costs and to benefit from the positive effects of recirculation. The aforementioned inorganic and organic load necessitate the use of PW treatment technologies. Biological processes such as anaerobic digestion proved to be feasible from various publications. Anaerobic degradation enables a reduction of chemical oxygen demand (COD) by up to 75% (Wirth et al., 2015). Another utilization pathway for PW is to recover nutrients from it. Malhotra and Garg, 2020 performed recovery of humic acids from PW using ammonium sulfate and were able to recover ~70% of humic acids. Subsequent growth trials showed positive effects (Malhotra and Garg, 2020). However, subsequent treatment of PW is necessary. Various providers of HTC solutions have their treatment technologies, like nanofiltration and reverse osmosis (Kläusli, 2014; Fettig et al., 2018) or aerobic treatment in a constructed wetland (Fettig et al., 2018). However, no data was available on the efficiency of these technologies and continuous large-scale operation is lacking. For a commercial realization of HTC technology, efficient and cost-effective processes for process water treatment are required.

2.4 Industrial readiness and industrial application

In addition to the mature technology, sufficient quantities of sewage sludge are required for the successful implementation of HTC technology for sewage sludge management and valorization in rural areas. The HTC technology must also be competitive with other thermal processes like incineration or pyrolysis to make its implementation successful. Reißmann et al., 2020 created a base model for HTC as a sewage sludge utilization method in Germany for 2030 assuming the currently best available techniques (BAT). In this model, 65,000 t FM sewage sludge per year is utilized (14,300 tons of dry matter per year with 22% DM). Due to the continuous industrial operation and the knowledge gained from it, learning effects can be observed in operational management. Nutrient recycling (e.g., phosphorus) is integrated in addition to the basic model. The authors concluded that production costs, phosphorus recovery, and process water treatment have a significant impact on the competitiveness of HTC compared to conventional processes such as incineration. According to this study, competitive production costs for the final HTC product must be less than € 325 per ton of hydrochar produced. Reißmann et al., 2020 point out that only the delivery of the product up to mono-incineration and not beyond was taken into account in this cost calculation. The HTC technology however has not yet (2023) been able to establish itself as a valorization process for the treated sewage sludge in Germany and especially for rural areas. The technology was temporarily tested on a sewage treatment plant in Düsseldorf but was discontinued after a test phase (Schnell et al., 2020). There are several methods for industrializing the technology at the moment, including multi-batch processes (quasi-continuous) and processes in tubular reactors (Blöhse, 2017; Quicker and Weber, 2016). There are some providers of commercial HTC solutions which in-

cludes TerraNova Energy, HTCycle, and SunCoal Industries (Aragón-Briceño et al., 2021).

3. HTC AND NUTRIENT RECOVERY

3.1 Need for phosphorus recovery and recovery technics

Phosphorus is a critical resource and a non-renewable essential element for all living organisms on the earth. The European Commission designated phosphorus as a "critical raw material" in 2014. (Wang et al., 2020; Aragón-Briceño et al., 2021). According to Krüger and Adam, 2015, more than 550,000 t/a of phosphorus was applied to German farmlands in 2015. The global phosphorus reserves are limited and the over-exploitation of natural reserves of phosphorus is anticipated to create severe problems in the next 50-100 years. Current phosphorus reserves are located in the US, Morocco, Jordan, China, and South Africa, assuming that Germany and Europe are entirely dependent on imports. The remaining phosphate reserves are however contaminated with heavy metals such as cadmium or uranium (Krüger and Adam, 2015). Various studies have assumed that the available phosphorus reserves will soon be exhausted (Pérez et al, 2021). Increasing population growth leads to higher consumption of energy and resources and to meet the phosphorus demand of the raising population, there is an immediate need for intelligent phosphorus recovery technologies and alternative sources of phosphorus. The integrated concerns such as; non-renewable nature, significance on global food security, and serious cost volatility, the future of phosphorus availability is drawing greater attention and poses an urgent need to find an alternative phosphorus source (Heckenmüller et al., 2014). As waste biomasses such as sewage sludge contain high phosphorus concentrations, several phosphorus recovery technologies are now available (Aragón-Briceño et al., 2021). The easiest way is land-based recycling with phosphorus being returned to the natural cycle. Rural areas in particular have benefited from land-based sewage sludge utilization. However, sewage sludge contains heavy metals and organic pollutants which makes the direct-recycling route more difficult (Aragón-Briceño et al., 2021). In this concern, the direct utilization of sewage sludge on agricultural land is prohibited. Several recovery technologies are based on the recovery of phosphorus from the sewage sludge ash, requiring incineration of the sewage sludge to produce phosphorus-rich ash (Kwapinski et al, 2021; Krüger and Adam, 2015). Hydrothermal carbonization in combination with subsequent phosphorus recovery would be an attractive option for rural regions without sewage sludge incineration (Kwapinski et al, 2021; Pérez et al, 2021).

3.2 Influence of acid utilization during HTC sewage sludge

3.2.1 Effects of Post- and Pre-Acid Treatment During HTC

HTC significantly reduces sewage sludge's acid buffering capacity due to the chemical reactions and thermochemical breakdown that occurs during the process. Carrying out acid leaching after HTC of sewage sludge, the majority of the H^+ in added acids will be utilized to induce the dissolution of Al-P and Fe-P and transformation of higher phosphorus from solid to liquid phase (Shettigondahalli et al., 2022). In contrast, when the acids are used during or before the HTC process, a significantly lower concentration of phosphorus will be transformed from the solid to the liquid phase. When acids are used before or during HTC, the majority of H^+ ions added in the form of acids are used to overcome buffering resistance provided by carbonates, cation exchange reactions, and organic matter. Due to the buffering agents present in the system, the available H^+ is greatly depleted before it can react with metal ions that hold phosphorus.

The presence of phosphate-precipitating metals such as Fe, Al, and Ca in sewage sludge plays a more significant role in determining the degree of conversion of phosphorus from solid to liquid (Huang et al., 2018; Ekpo et al., 2016). The presence of multivalent metal ions such as Al^{3+}, Ca^{2+}, Fe^{3+}, and Mg^{2+} during the HTC of sewage sludge contributes to the formation of phosphate with low solubility, which then facilitates the accumulation of phosphorus onto hydrochar. Similarly, the acid buffering resistance of the sewage sludge also regulates the phosphorus transformation from the solid to liquid phase upon the addition of acids. Sewage sludge suspension in general consists of a liquid and a solid phase. The solid and liquid phase of the sewage sludge contains several compounds with a high tendency to inhibit acidification (Shettigondahalli et al., 2022). The acid-inhibiting substance present in sewage sludge suspension tends to have different neutralizing points. Upon adding acids to sewage sludge suspension, H^+ would initially react with carbonates existing in the sewage sludge with relatively higher neutral points in the suspension. The additional H^+ will undergo a cation exchange after the carbonate in sewage sludge is exhausted. Later the presence of additional H^+ would be consumed in offsetting the buffering resistance provided by organic matter present in sewage sludge. In the end, the presence of any further H^+ would be utilized in the dissolution of aluminum phosphates (Al-P) and ferric phosphates (Fe-P) (Zhang et al., 2010; Bozkurt et al., 2000; Petzet et al., 2012). The HTC process however contributes considerably to reducing the acid buffering capacity of sewage sludge. By acid leaching the sewage sludge after HTC, there will be maximum utilization of added acids to induce the dissolution of Al-P and Fe-P and significantly increase the phosphorus-leaching from the solid to the liquid phase.

3.2.2 Recovery of Phosphorus from HTC-treated sewage sludge hydrochar

The utilization of H_2SO_4 and HCl at higher concentrations increases the mobilization of phosphorus (80-100%) from the solid to the liquid phase in hydrochar derived from sewage sludge (Pérez et al., 2021). Phosphorus leaching and the subsequent mobilization of heavy metals from hydrochars were investigated by Pérez et al., 2022, using oxalate and citrate across a pH range of 0 to 4. Oxalate resulted in nearly full P release from hydrochars at pH 1, whereas both oxalate and citric acids achieved P extraction efficiencies that were better than 75% even at

the lowest pH. Acid leaching of the sewage sludge hydrochar results in a high phosphorus and multivalent cation recovery. Nevertheless, heavy metal concentrations must be monitored throughout the process since they affect the product's potential use as fertilizer. According to Gerner et al., hydrochar has an affinity towards heavy metals and will retain a significant portion of them, releasing very little into the liquid phase. The presence of a higher concentration of heavy metal in hydrochar makes the land-based application restricted under the German Fertilizer Ordinance. The most practical use option is then the energy recovery from hydrochar. HTC process also transfers around 50% of nitrogen from the solid to liquid phases, increasing hydrochar combustion performance in terms of NO_x emissions reduction (Gerner et al., 2021).

Calcium phosphate salt is a desirable product for recovering phosphorus from leachate. Calcium phosphate is similar to phosphate rock, the primary basic material for the fertilizer industry. The phosphorus product extracted from the effluent can be incorporated directly into the process as a by-product. The filtrate after leaching is believed to have a high ionic strength, which influences ion-association and solubility. Due to the decreased concentration of free ions caused by ion association, supersaturation may be required for the formation of solid deposits (Ehrnström, 2016). In order to recover all dissolved phosphorus, excess calcium ions must be introduced to the leachate. Increasing the pH could have a comparable effect.

4. CONCLUSIONS

The use of agriculture and landscaping as traditional treatment methods will soon be phased out in Germany due to new regulations on the management of sewage sludge (2029). Rural areas where sewage sludge is usually disposed of by agriculture and landscaping will be particularly challenged by the forthcoming situation. Hydrothermal carbonization (HTC) is receiving increased attention as an eco-friendly and promising technology for treating and managing sewage sludge without the need for drying. It is possible to effectively manage sewage sludge by using HTC technology not only by recovering phosphate but also by complying with German Sewage Sludge Ordinance requirements. HTC offers major potential for the valorization of sewage sludge and could be an interesting alternative for sewage sludge treatment and nutrient recovery in rural areas of Germany. Especially for nutrient recovery, HTC could be an opportunity to close loops. However, sufficient quantities of sewage sludge are needed to enable continuous operation. The HTC plant with subsequent process water treatment and nutrient recovery facilities should be built on the site of a WWTP to enable indirect discharge of pre-treated PW. The HTC process water is another challenge, as significant amounts are produced during continuous operation. The PW is organically contaminated and has to be treated before discharge into the environment. A functional and eco-economic concept for PW-management is necessary for a commercial implementation of HTC technology. Future research should focus on methods to minimize the amount of heavy metal in hydrochar and its use as fertilizer in accordance with the legal requirements of the German Fertilizer Ordinance and other relevant regulations. The technology has not yet (2023) been able to establish itself in an industrial continuously operated HTC plant for sewage sludge utilization in Germany. The technology readiness to manage and handle process water produced from HTC of sewage sludge is the major concern. A practical, dependable, and affordable process water disposal method is essential for the successful commercialization of HTC technology. Given the current rate of scientific development in the area, this is probably anticipated to happen in the near future.

AUTHORS CONTRIBUTION

Vicky Shettigondahalli Ekanthalu and Tommy Ender contributed equally to every aspect of this article until it was accepted and published online. Michael Nelles was responsible for reviewing and editing aspects of this article.

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Extra contents

COLUMNS AND SPECIAL CONTENTS

This section comprises columns and special contents not subjected to peer-review

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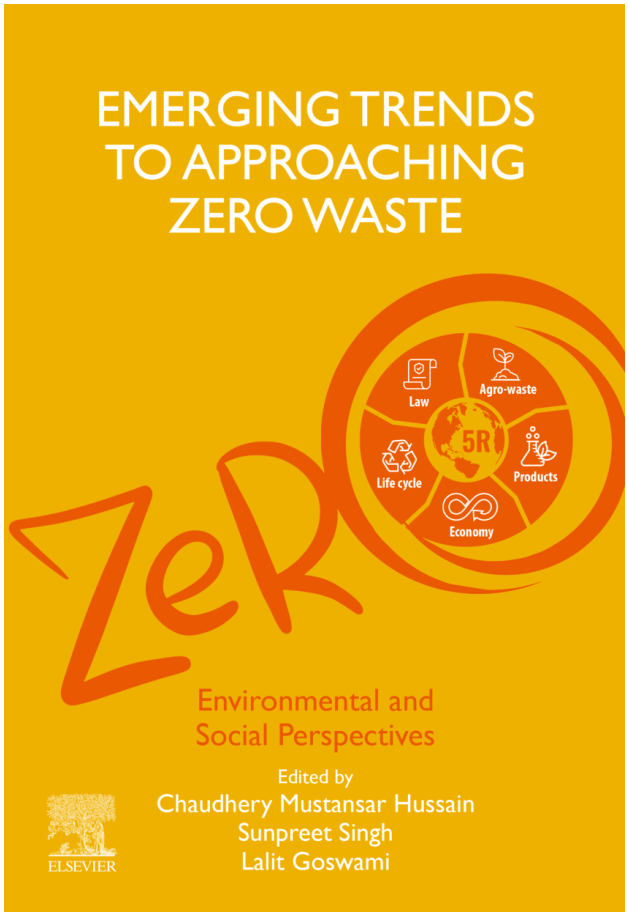
BOOKS REVIEW



EMERGING TRENDS TO APPROACHING ZERO WASTE

Edited by: Chaudhery Mustansar Hussain, Sunpreet Singh, Lalit Goswami

The book "Emerging Trends to Approaching Zero Waste" is a collection of contributions that shed light on different possible approaches for waste minimization and, ideally, zero waste production. Strategies to approach zero waste generation have been studied and continuously proposed since the end of last century, with a number of publications on this topic that has grown exponentially, following the same pattern of the academic works on circular economy, whose principles are tightly connected to the zero-waste concept. However, the achievement of zero-waste targets is hindered by many political, cultural and industrial barriers. The topic investigated in the book is therefore challenging, but many solutions proposed by the authors could be successfully applied both to India (the affiliation country of the authors) and globally.

The book is divided into 16 chapters written by 43 contributing authors. Each chapter either contains dissertations on general, organic and policy-driven approaches that may facilitate the achievement of zero-waste targets or discusses specific examples of strategies that could be implemented locally or globally.

Chapter 1 starts with the definition of "zero waste" given by the Zero Waste International Alliance, i.e. "the conservation of all resources by means of responsible production, consumption, reuse and recovery of products, packaging and materials without burning and with no discharges to land, water or air that threaten the environment or human health", prevention being the priority target rather than reuse or recycle. Soon after, the focus moves to zero-waste principles in the construction and demolition sector. An initial characterization of the different types of construction and demolition waste (CDW) and the related processes that generate it is followed by the presentation of the current practices for CDW minimization, conversion to energy, software-aided smart management, assessment tools (e.g.: Life Cycle Assessment), recycling and recent policies set by governments for sustainable construction. The chapter discusses the main challenges towards zero CDW generation, including the costs of sustainable buildings and the consequent low level of acceptance by stakeholders, favored by the lack of policies in many countries.

Chapter 2 focuses on rural indigenous populations in India as an example of communities historically devoted to sustainability, nature preservation, and waste reduction, reuse and recycling, i.e. concepts that seem relatively new to current generations but that have their roots in pre-industrialized communities worldwide. The chapter recalls the principles of Hindu philosophy, stressing the importance that Indian populations have given to environmental sustainability.

Aquaponics is the subject of Chapter 3. Aquaponics is a natural food-growing method based on the symbiosis between fish, plants, bacteria and other organisms. Such method does not require the use of fertilizers, does not generate waste and produces fish and vegetables in a sustainable and safe way. The chapter describes the aquaponic process detailing the different phases: fish feeding, microbial conversion of fish waste (nitrification), absorption of nutrients from the root systems of plants and return of clean water to the system.

Chapter 4 is a review of Indian regulations and policies on waste management. The review recalls the waste management system in India, the bodies involved, the main reg-

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ulations on sanitary landfilling, but also the main barriers towards the full compliance with the regulations, especially the lack of laws on the selective collection of waste, improper behaviors by users, the fractionation of India in its federal structure and the low level of e-waste recycling in industries. The ideal zero-waste target is extremely challenging in big Indian cities, as the authors conclude that an appropriate legislation supporting the achievement of zero-waste targets is lacking in India. However, virtuous examples of Indian regions and other international locations attaining high selective collection rates (> 90%) are presented and discussed.

The focus of Chapter 5 is on the recent advances in technologies for the valorization of agricultural and food wastes. The chapter starts with an introduction on the environmental issues caused by the exponential increase in the global population and the consequent production of agricultural and food waste, which, if not properly managed, are significant contributors to greenhouse gas emissions. The chapter then focuses on the possible solutions for a correct management of biodegradable waste. Thermochemical (pyrolysis, gasification, torrefaction, hydrothermal carbonization and supercritical fluid extraction) and biological technologies (anaerobic digestion, enzymatic hydrolysis and fermentation) for food and agricultural waste management are discussed in detail, including the products that can be obtained in biorefineries, and the main advantages and disadvantages of each process are presented.

Chapter 6 deals with the remediation of a specific pollutant category in wastewater: chlorinated organic compounds (COCs), i.e. persistent organic pollutants like polychlorinated phenyl, chlorobenzenes, polychlorinated alkanes, polychlorinated alkenes and polychlorinated phenols, used in many industrial applications. The authors present the origins of COCs and their effects on human health. Most of the chapter is dedicated to a detailed presentation of the removal technologies that can be applied to wastewater. Besides conventional (adsorption) and established methods (membrane separation, advanced or electrochemical oxidation, cold-plasma discharge), novel options are presented, based on catalysis. Specifically, catalytic process involving zero-valent metals and transition metal oxides, the latter also used as photocatalysts. Nanocomposite materials based on metal oxides have shown great potential for COC removal at accessible costs.

Chapter 7 firstly describes the zero-waste concept, stressing the importance of re-designing production and supply chains rather than investing in reuse or recycling. Afterwards, the chapter focuses on the role of non-governmental organizations (NGOs) in promoting a zero-waste culture and, in some contexts like India, contributing to the achievements of targets that municipalities cannot reach alone, like door-to-door collection, promoting producers' responsibility, promoting awareness campaigns among citizens or employing waste pickers as specialized waste-management personnel. Specific examples of Indian NGOs operating in the field of waste management are given.

Chapter 8 discusses the role of carbonaceous materials in the removal of pharmaceutical and personal care products (PPCPs) from wastewater. The authors firstly present the origin, physical and chemical properties, toxicity, fate and typical concentrations of the most common PPCPs found in water environments, including wastewater treatment plants (WWTPs). In the second part of the chapter, carbonaceous materials (activated carbon, carbon nanotubes, graphene and derivatives, biochar and mesoporous carbons) and their effectiveness in removing specific PPCPs are reviewed. The authors conclude that activated carbon is still the preferred option due to its price and its well-known properties.

In the following chapter (Chapter 9), the authors analyze the factors influencing household waste management from the social and cultural points of view. Specifically, the selective collection rate at home is influenced by social factors like demographic characteristics of the users, the users' psychology (e.g., required effort and sensitivity to environmental issues), economic convenience and the level of compliance with existing policies. Strategies to improve household waste management include the involvement of NGOs, persuasive communication, investing in public education and any other measure to facilitate separate disposal of waste (e.g., strategic placement of waste bins, providing a positive image of waste management officials). The chapter ends with considerations on the potentials of Internet of Things for supporting waste collection.

Chapter 10 deals with the recent advances in the fashion and textile industries in terms of product sustainability and waste management. This sector generates 2.1 billion tons of clothes disposed of every year and is considered as the second main contributor to the global environmental impacts after the oil industry. The concepts of zero-waste fashion (i.e. a way of producing textiles that makes use of techniques allowing for no discard of textiles) and re-fashion (i.e., the reuse and upcycling of used clothes) as well as the role of fashion designers are then discussed. Afterwards, the authors present possible recycling pathways, including fabrics to fabrics, plastics to fabrics, food/agricultural waste to fabrics and leather, and fabrics to construction materials. However, due to the high costs currently involved, the market is still not ready to accept the complete reprocessing of clothes.

Chapter 11 focuses again on agricultural waste, but with the purpose of exploring the current barriers in waste management. The chapter presents the unexploited great potentials for fuel and energy production of the agricultural waste produced in USA, Africa, Asia and Europe. The authors then review additional biological treatments (solid-state fermentation for the production of enzymes, antioxidants and antibiotics, dark fermentation for hydrogen production, composting, vermicomposting and larvae-mediated bioconversion to produce biofertilizers and animal food) and chemical treatments (acid/base-catalyzed transesterification to produce biodiesel from oils and fatty acids). The authors identify logistics and its economy as the biggest hurdles in agricultural waste management. Increasing energy efficiency, subsides and policies from governments, strategic location of biorefineries and promoting awareness on the value of agricultural waste are regarded as key steps to support a circular economy in this sector.

Though not directly related to the zero-waste concept, Chapter 12 introduces the ongoing research on ammonia (NH_3) synthesis, intended as a sustainable carrier of renewable energy. Specifically, NH_3 can be produced through different approaches, namely homogeneous catalysis, heterogeneous catalysis and electrochemical methods exploiting renewable energy sources that are not constant by nature (e.g., photovoltaic and wind energies). The first two routes are particular promising in terms of reaction rates and selectivity, providing that catalyst durability is improved and costs are reduced.

Chapter 13 deals with the management of solid waste through the zero-waste concept. Solid waste is reviewed as a potential source for different purposes: food waste can be used for the production of bioenergy; food, plastic, electronic and industrial (e.g., waste tyres) waste can be used for the production of intermediate materials for energy storage and conversion (e.g., carbonaceous materials, sunlight conversion films); plastic waste can be used as construction materials (blocks, bricks, flooring, wood walls or pavements); plastic waste and fly ash can be used in cementitious composites; plastic, agricultural and textile waste may be used as insulation materials; food and agricultural waste can be converted into biodegradable bags, films and packaging materials. The main barrier is represented by the need for a very efficient selective collection system, since waste separation at the source is essential to avoid material contaminations.

Economic aspects related to waste management are discussed in Chapter 14. Figures on the global market values of municipal solid waste, electronic waste, plastic waste, hazardous waste, automobile waste and waste-to-energy streams are given. The authors review the factors influencing the failure of the waste market under a zero-waste perspective: the absence of governance and policy interventions (e.g., landfill taxation schemes and support to sustainable production and reuse/recycling strategies), illegal waste dumping and a lack of planning regarding infrastructures. Recycling would create jobs and revenue and, thus, it represents a great opportunity for every country. The authors present the Life Cycle Cost analysis as a useful tool for both economic and environmental perspectives regarding recycling. Afterwards, the focus moves to policy instruments, which are crucial to ensure the transition towards a circular economy. The authors start describing the challenges in developing countries, mainly related to lack of public financial resources to support the private sector. Then, some policy instruments are presented: compulsory recycling of recyclable materials, fees for residual solid waste production, communication campaigns, subsides and green public procurement.

Chapter 15 highlights the role of microalgae in the production of biofuels, food and valuable chemicals. This interest is justified by the potentials of microalgae: indeed, the mass-specific assimilation of CO_2 by microalgae is about 200 times higher than other plants and microalgae do not require freshwater or cultivable land. The main microalgae constituents, products and their uses are listed. Opportunities for the direct utilization of secondary products and the methods for their conversion are reviewed. In addition, the authors present in detail the best approaches available in microalgae biorefineries, focusing on closed-loop and self-sustainable models, which make biorefinery processes viable also from the economic point of view. Furthermore, different available options for the sustainability assessment of microalgae biorefineries are presented: Life Cycle Assessment, techno- and socio-economic analyses and multi-criteria decision analysis.

The last section (Chapter 16) focuses on the removal technologies of melanoidin from wastewater. Melanoidin is released by distillery, fermentation, coffee extraction and pharmaceutical industries. Once in the environment, it may form stable complexes with metal ions, reduce soil alkalinity and the availability of magnesium. In the first part of the chapter, the main sources and properties of melanoidin are presented, including its genotoxicity and cytotoxicity. Furthermore, physicochemical (coagulation, flocculation, electrocoagulation, adsorption and membrane filtration) and biological (anaerobic digestion, bio-trickling filtration, bio-oxidation and constructed wetlands) treatments, with their advantages and disadvantages, are discussed in detail. A combination of physicochemical and biological treatments, rather than single processes, allows for the best results in melanoidin removal. Finally, recovery options for the reuse of melanoidin in the production of cosmetics and biosurfactants are presented.

Overall, although some chapters are specifically dedicated to recycling, renewable energies and remediation techniques more than waste prevention, the book provides the readers with interesting examples of zero-waste approaches in several production sectors, policies and socio-economic tendencies that have been or are currently applied in different countries, highlighting differences between developed and developing countries.

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DETRITUS & ART / A personal point of view on Environment and Art

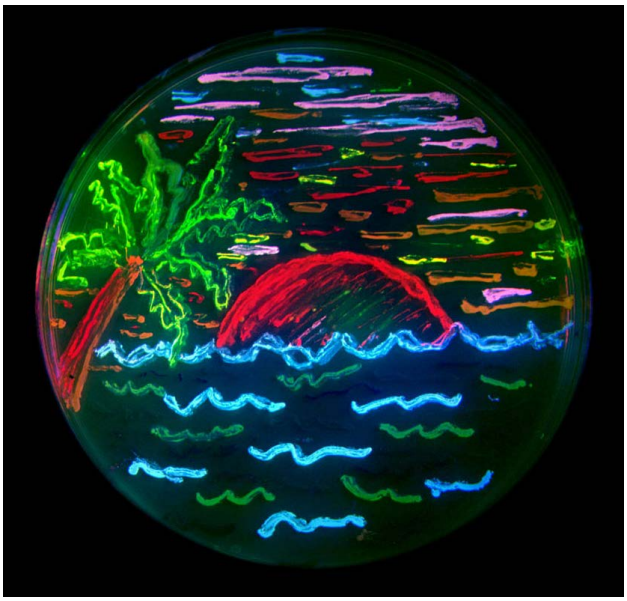
by Rainer Stegmann

Recently I came across Bacterial Art also called Microbial Art. I had never heard about it before. To get an idea what it is I asked "Big Brother" Chat AI GPT and I got an excellent answer. I present some excerpts:

"*Ah, bacterial art a fascinating and creative intersection of science and art! Artists harness the natural abilities of bacteria to grow and form intricate patterns. They carefully manipulate the growth conditions, such as temperature, nutrients, and agar medium, to guide the bacteria's growth and create desired shapes and colors. The result is a mesmerizing display of living art. One popular technique in bacterial art is called "bacterial painting." Artists use a sterile brush or other tools to apply different strains of bacteria onto a solid surface, such as agar on a petri dish. As the bacteria grow and spread, they cre-ate vibrant and intricate patterns (*Example No. 1). *Another technique involves using genetically modi-fied bacteria that produce pigments or fluorescent proteins* (Example No. 2). *Bacterial art not only showcases the aesthetic beauty of microorganisms but also raises awareness about the importance of bacteria in our lives*". It is a bit frightening this Chat AI GPT, thinking about the amazing potentials; but the text must be checked for errors.

I like the analogy that agar plates may be the canvas of the "painter", while the specific bacteria and yeasts represent the paint. The art work can be sealed -after their sufficient incubation- with epoxy. The bacteria, yeast, or fungi are chosen for their natural colours as Bacillus subtilis (cream to brown), Chromobacterium violaceum (violet)" and others (based on Wikipedia).

EXAMPLE 1 / Art work from the series Seascapes (courtesy of Dr. Mehmet Berkmen) www.bacterialart.com



EXAMPLE 2 / Artwork by Nathan Shaner, photography by Paul Steinbach, created in the lab of Roger Tsien in 2006. CC BY-SA (from Wikipedia)

A very active group in this field is chaired by Dr. Mehmet Berkmen. Together with the local artist Maria Peñil Cobo, the Berkmen Lab has the mission to bridge the gap between Arts and Sciences, and be-tween Humans and Microbes. The Berkmen Lab has engaged local schools in STEAM events, orga-nized workshops at universities, presented their work in international conferences and presented their work in galleries. (modified from https://international.neb.com/research-labs/berkmen-lab/research-projects/bacterial-art). Dr. Berkmen and I realized that we both have the same motivation using art to make disciplines more visible and enjoy their beauty. He gave us permission to publish this beautiful artwork No.1 from the series "Seascapes" on our page. For those of you getting more interested in this art direction should visit beyond others the website https://www.bacterialart.com.

I found another example of Bacterial Art on Wikipedia: Beach scene with bacterial strains expressing different kinds of fluorescent proteins, from the laboratory of the Nobel Prize–winning biochem-ist Roger Tsien (Example 2).

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Now we come to the obvious connection of bacterial art and waste management (WM). Biological waste treatment is one of the pillars of WM. Bacteria operate the biological degradation of organics during composting and the acidification and acetogenesis under anaerobic conditions; they are also active in biofilters, landfills, during biological contaminated soil treatment and other WM areas. Bacteria are not visible during practical application in biological plants; i.e., for non- biologists there is a re-strained relationship to the specific bacteria. I think, through the representation of bacterial art more in-terest for the microbiology of bacteria may be raised. Engineers use biological processes in WM all the time and can control the processes very well without decent knowledge about the specific bacteria in-volved. So, why should we know more about them. I think for the further improvement of the biological processes in WM and the extension of their application (e.g., microbiological production of specific organic acids and hydrogen) the engineers have to cooperate with the microbiologist. But this is only successful when there is a basic microbio-logical knowledge so that both disciplines can communicate with each other. I see also potentials in biological waste treatment by developing gene manipulated bacteria. Interesting for our field would be a faster biological methane oxidation in biofilters, and may be designed specialized bacteria for the deg-radation of halogenated multi- ring aromates that are not supplanted by the existing microorganism. Well, there are more potentials we can think of, but we have to make sure that we do no not open Pandora´s box.

Let us admire the amazing creativity of the bacterial art artists and enjoy the beauty of their creations. May be some of us get inspired for new activities.

In the next issue I will present a sculpture by Umberto Boccioni (1882-1916) "Dynamism of a Speeding Horse + Houses". Boccioni was an Italian painter and sculptor. He was a representative of the movement Futurism.

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