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PYROLYSIS OF PELLETS PREPARED FROM GROUNDNUT SHELL AND CRUDE GLYCEROL: IN-SITU UTILIZATION OF PYRO-GAS AND CHARACTERIZATION OF PRODUCTS

Mayankkumar Parmar [1,2], Bhavin Soni [1], Arth Jayesh Shah [1] and Sanjib Kumar Karmee [1,*]

[1] *Thermo-Chemical Conversion Division, Sardar Patel Renewable Energy Research Institute (SPRERI), Vallabh Vidyanagar, 388 120, Anand, Gujarat, India*
[2] *S.N. Patel Institute of Technology and Research Centre, Umrakh Vidyabharti Campus, Bardoli - 394601, Surat, Gujarat, India*

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ABSTRACT
During biodiesel production process crude glycerol (a polyol) is obtained as a by-product. In this paper, an effort has been made for using it for pellet production from groundnut shell. Three types of pellets containing 20 wt%, 40 wt% and 60 wt% crude glycerol were prepared. Palletisation led to easy handling of biomass and also increases energy density. Furthermore, characterisation of prepared pellets was performed and subsequently, pyrolized. An increase of volatile matter from 72.45 wt% to 85.18 wt% in pellets was noted with addition of glycerol. Firstly, pyrolysis of groundnut shell pellets was carried out in batch (0.5kg) at the temperature range of 400°C to 600°C with the step size of 50°C. From these experiments the maximum yield was obtain at 550°C. Therefore, pyrolysis of glycerol containing pellets was carried out at optimum temperature of 550°C along with in-situ circulation of generated pyro-gas. Bio-oil yield increased from 30 wt% to 41 wt% in batch scale as glycerol content increased from 0 wt% to 60 wt%. Pyrolysis products were thoroughly characterised to understand the effects of crude glycerol addition. Calorific value of bio-char was increased from 20.89 MJ/kg to 23.67 MJ/kg as glycerol content increased. Calorific value of bio-oil was 32.66 MJ/kg. The pyro-gas produced was utilized to heat the pyrolysis reactor. Pyro-gas yield increased from 28 wt % to 32 wt% in batch scale as glycerol content increased. In-situ utilization of pyro-gas led to ~ 17% electricity saving.

1. INTRODUCTION

Different fossil fuels viz. petrol, diesel, kerosene, heavy oil and coal are extensively exploited for energy generation. Along this line, conventional fossil fuels reserves are limited resources and geographically located only in few countries. During burning of fossil fuels CO_2, CO, SO_x, NO_x and CH_4 are being emitted (UNECE Methane Management, 2020). It is a known fact that fossil fuel burning causes deteriorationsof air quality; which is leading to health and environmental concerns. In this context, there is a need to develop non-conventional energy sources. In this context, biofuels prepared from wastes are potential candidates.

Biomass is a versatile, abundant and low-cost feedstock. In particular, waste biomass, for instance, agro-residues, forestry residues and organic portion of municipal solid waste (MSW) are abundantly available. If these wastes are dumped in landfills; they will emit methane and simultaneously generates leachate. Methane is a potent GHG which is 84 times more harmful than CO_2 (UNECE Methane Management , 2020).

In India, ~500 million metric tonnes of agro residues are available according to 2019 data (Renewable Energy Government of India, 2019). Among the crops cultivated in India, groundnut (Arachis hypogaea) is a major one. According to 2018-19 data, worldwide India is the second largest producer of groundnut (Directorate of economics and statistics Government of India, Kharif Survey, 2018). In India, production of groundnut was 51.93 lakh metric tonnes and 68.59 lakh metrics tonnes in the year 2018 and 2019 respectively (Directorate of economics and statistics, Government of India, Kharif Survey, 2018). Groundnut plays a vital role in supporting the edible oilseed economy of India. Furthermore, groundnut is also used for production of salted peanuts, peanut butter, peanut flour, protein supplements, and vegetable ghee. Every year, global production of groundnut is increasing at 1.11% rate because of its high consumption with improved living standards (Directorate

* Corresponding author:
Sanjib Kumar Karmee
email: sanjibkarmee@gmail.com

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of economics and statistics Government of India, Kharif Survey, 2018).

In groundnut, the shell accounts for ~20 wt% of complete peanut pod (Duc et al., 2019). According to an estimation, India generated ~13.718 lakh metrics tonnes of groundnut shell (GNS) (according to 2019 data). Presently, GNS is largely burnt in loose form to generate thermal energy (Duc et al., 2019). Loose biomass combustion has limitation and it is environment unfriendly. Therefore, it needs to be valorised in a sustainable manner. In this regard, densification is an excellent approach for conversion of loose groundnut shell into pellets. Pelletization of agricultural residues like groundnut shell of the utmost importance from circular economy and waste management perspectives.

To meet the growing demand of liquid fuel, biodiesel production is increasing drastically. During the preparation of biodiesel ~ 10 wt% of crude glycerol is formed as a by-product. Annually ~16.1 million tonnes of crude glycerol are generated through biodiesel production process. The obtained crude glycerol can be used in food, cosmetics and drug industries but needs extensive purification to remove impurities like residual soap, methanol, ester, oil, catalyst, water and other impurities (Bartocci et al., 2018). Purification of crude glycerol is rather difficult and costlier affair. However, crude glycerol can be used as an additive along with agro-residues for production of pellets (Paulauskas et al., 2015).

(Abdul Hai et al., 2021) reported that pyrolysis of groundnut shell (GNS) was processed at 500°C in an inert gas flow rate 10 mL/min and heating rate 10°C/min, respectively, in fluidized bed pyrolysis-reactor and the generated oil yield was 62.8 wt%; whereas, biochar and biogas yields were 19.5 wt% and 17.7 wt% respectively. A study on pyrolysis of GNS at 650°C produced 30 wt% of biochar, 25 wt% of bio-oil and 45 wt% of pyro-gas (N. Radhakrishnan and V.Gnanamoorthi. 2015).

In this study, pellets (6 mm diameter) were produced using solid (groundnut shell) and liquid wastes (crude glycerol) by mixing in different ratios: GNSP00, GNSP20, GNSP40 and GNSP60. Afterwards, the obtained pellets were valorised through batch scale pyrolysis to generate bio-oil, bio-char and pyro-gas. To demonstrate the potential of sustainable waste management and zero-waste process, pyro-gas was utilized in an in-situ manner for heating of the reactor. Electrical energy saving up-to 17% was observed during batch scale pyrolysis mode. Yield of pyrolysis products remain unaffected for experiments with utilization of pyro-gas.

1.1 Abbreviations

GNS	Groundnut Shell
GNSP00	Pellets produced from only Groundnut Shell
GNSP20	Pellets produced from a mixture of Groundnut Shell (80 wt%) and crude Glycerol (20 wt%)
GNSP40	Pellets produced from a mixture of Groundnut Shell (60 wt%) and crude Glycerol (40 wt%)
GNSP60	Pellets produced from a mixture of Groundnut Shell (40 wt%) and crude Glycerol (60 wt%)
GNSPC00	Bio-char of GNSP00
GNSPC20	Bio-char of GNSP20
GNSPC40	Bio-char of GNSP40
GNSPC60	Bio-char of GNSP60
GHGs	Green House Gases
ASTM	American Society of Testing Material
TGA	Thermo-gravimetric analysis
MSW	Municipal Solid Waste
PID	Proportional Integral and Derivative
CV	Calorific Value
ASAE	American Society of Agriculture Engineering
FT-IR	Fourier Transform-Infrared
GC-MS	Gas Chromatography-Mass Spectrometry
NMR	Nuclear Magnetic Resonance
Na_2SO_4	Sodium sulphate

2. MATERIALS AND METHODS

2.1 Material procurement and characterisation

GNS was purchased from Darshan Seeds Industries, Modasa, Gujarat, India. Initially Moisture content in the Raw GNS was 10.5 wt% which was measured using an infrared moisture analyzer (Sartorius® MA 100Q). Before pelletization, GNS was processed (ground) using a hammer mill. Crude glycerol was obtained from Fame Biofuels Pvt. Ltd, Manjusar GIDC, Savli road, Manjusar, Vadodara, Gujarat. The obtained crude glycerol was a by-product of biodiesel production process.

Characterization of the crude glycerol was carried out for determination of volatile content (wt%), ash content (wt%), sodium (Na) (wt%), Potassium (K) (wt%), methanol content (wt%), water content (wt%) and salt content (wt%) and were found to be 91.0%, 7.50%, 0.53%, 3.40%, 0.09%, 0.87% and 5.90% respectively. It was carried out at Microtek Research and Analytical Lab, Vadodara, Gujarat, India.

Proximate analysis of processed GNS was carried out in-accordance with ASTM standards. ASTM E-871 for moisture content, ASTM D-1102 for ash content, and ASTM E-872 for volatile matter were used for analysis (Basu. P Biomass gasification, pyrolysis and torrefaction: Practical design and theory, 2018). Fixed carbon content was measured by balance. These analyses were carried out at the Thermo-Chemical Conversion Technology (TCCT) Division, SPRERI using different instruments, namely, an infrared moisture analyzer (Sartorius® MA 100Q) for the measurement of moisture content and a muffle furnace attached with a PID temperature controller was used to estimate ash and volatile matter content. The analysis revealed that moisture content was 5.65 wt%, ash content was 8.48 wt%, volatile matter was 73.31 wt% and fixed carbon was 12.56 wt%.

The bulk density of GNS was determined using ASTM E-873-06 standard. Calorific value of the GNS was measured using an Automated Bomb Calorimeter (IKA® C 5000 cole-Parmer®, USA) located at the instrumentation laboratory of Thermo-Chemical Conversion Technology (TCCT) Division, SPRERI. The results indicate that bulk density was 170.25 kg/m^3, calorific value was 15.07 MJ/kg, and energy density was 2,565.66 MJ/kg.

Ultimate analysis of GNS was performed at the Sophisticated Instrumentation Centre for Applied Research and Testing (SICART), Vallabh Vidyanagar, Anand, Gujarat, In-

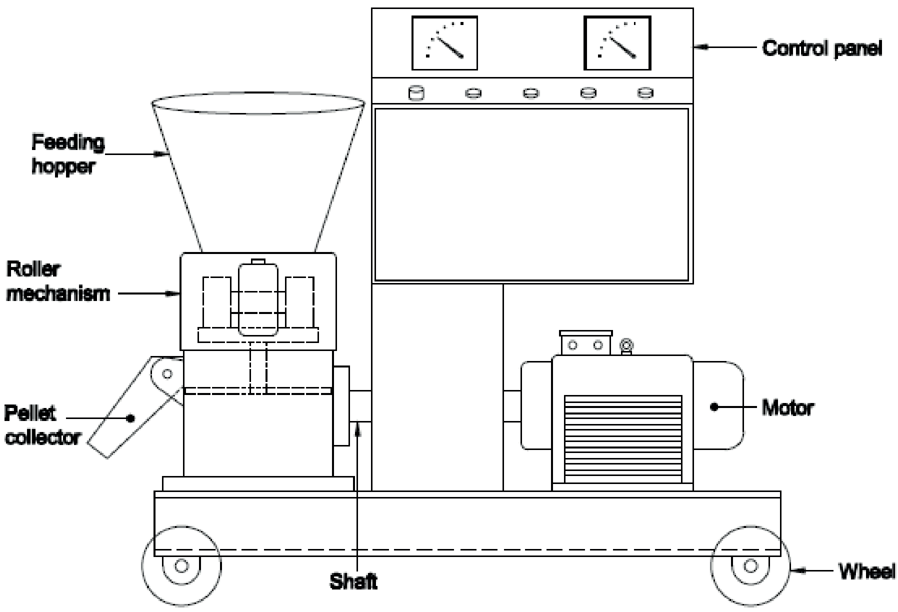

FIGURE 1: Pellet making machine used in this research.

dia. An Elemental Analyser (2400 series II, Perkin Elmer, USA) was used for this experiment.

As per the ultimate analysis Carbon (C), Hydrogen (H), Nitrogen (N) and Oxygen (O) content in GNS were 42.38 wt%, 5.97 wt%, 0.26 wt% and 51.39 wt% respectively. The Oxygen (O) content was calculated by balance. Similar results were reported by Bai et al. who reported moisture, ash, volatile matter and fixed carbon content as 4.89 wt%, 9.27 wt%, 72.90 wt% and 15.40 wt% respectively in groundnut shell; whereas Carbon (C), Hydrogen (H) and Nitrogen (N) content were 46.00 wt%, 5.45 wt%, 1.02 wt% and 47.13 wt% respectively (Bai et al., 2017). Carbon content in GNS was 42.02 wt% as reported by Collins et al. (Collins et al., 2018).

2.2 Pelletization

Production of the pellets (6 mm diameter) from groundnut shell (GNSP00) as well as from the mixture of GNS and crude glycerol (GNSP20, GNSP40 and GNSP60) were carried out at the TCCT Division, SPRERI, by using a pellet making machine (Capacity 20 kg/hr) (Figure 1). The pelletizer was procured from Vidharbha sales, Nagpur, Maharashtra, India.

Before feeding the mixture into the pelletizer, Die and Roller were lubricated and pre-heated (~70°C). Accordingly, mixture of groundnut shell (particle size ≤ 2mm) and Jatropha oil (in equal proportion) was used for lubrication and pre-heating. The temperature was measured using an Infrared Thermometer gun. In every mixture, water (as moisture) was added (10-15 wt% of total mixture). The obtained pellets were naturally dried for 12-15 hours. The material was stored for further characterisation and utilisation.

The first type of pellets i.e., GNSP00 was prepared with only GNS and water. While, three other types of pellets were generated by using processed GNS, water and crude glycerol by changing the composition (ratio) of GNS and crude glycerol in 80:20, 60:40, and 40:60 proportions. Before mixing of both materials, the crude glycerol was pre-heated in a water bath at ~ 60°C. Subsequently, the mixture was feed into a pelletizer and the densified fuels were obtained.

2.3 Characterisation of pellets

2.3.1 Proximate analysis, bulk density, calorific value and ultimate analysis

Proximate analysis, ultimate analysis, bulk density and calorific value of the pellets were measured as per methods discussed for the loose GNS (in section 2.1).

2.3.2 Durability

Durability of the pellets was measured according to ASAE S269.4 standard by using the tumbling apparatus made-up of rectangular container of stainless steel with internal volume of 300×300×125 mm^3. A batch of pellets sample (0.5 kg) was kept in a container and then tumbled for 500 rotations in 10 minutes.

2.3.3 TGA Analysis

The thermal induced weight loss behaviour of pellets was analyzed using a Perkin Elmer analyzer (Pyris-1 TGA, Perkin Elmer, USA; N_2 atmosphere, sensitivity: 0.0001 mg). Experiments were performed at the SICART, Vallabh Vidyanagar, Anand, Gujarat, India. During the analysis, 10 mg of material was heated under N_2 from 50°C to 1000°C (at 10°C/min).

2.4 Pyrolysis of pellets

A batch scale pyrolyzer unit (capacity: 0.5 kg) is designed and developed by the TCCT Division, SPRERI. It was used for conducting the experiments (Figure 3).

The reactor is made up of SS304. A hopper was attached with the unit for feeding of pellets into the reactor.

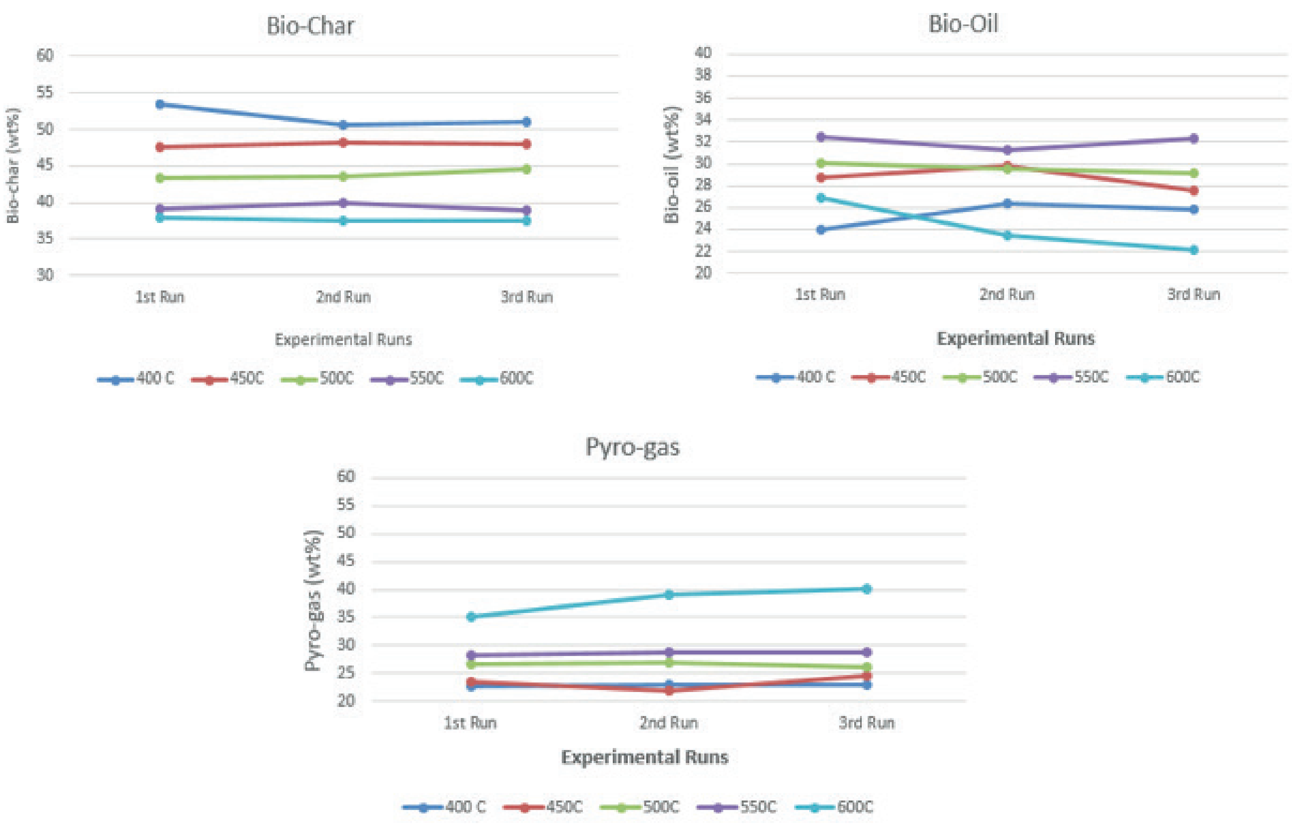

FIGURE 2: Experimental Run of Pyrolysis.

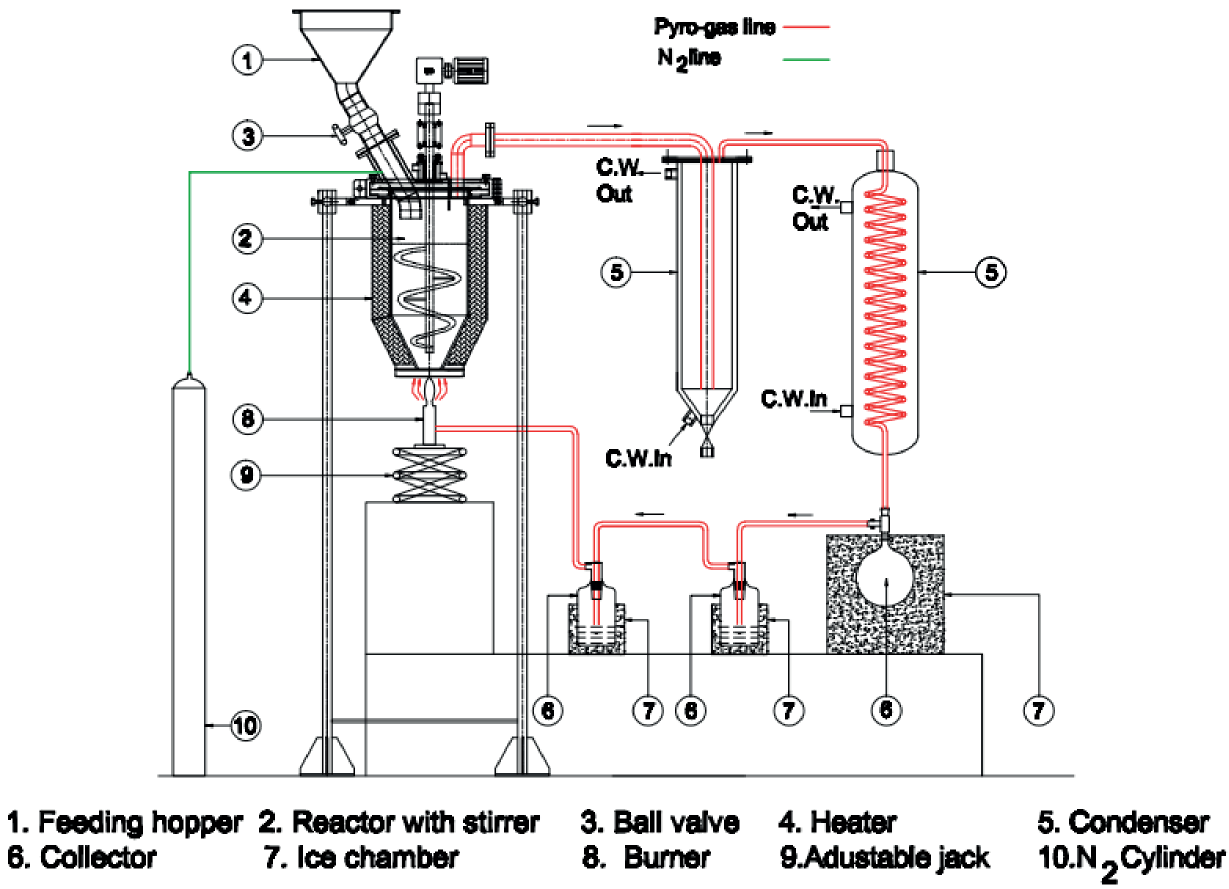

FIGURE 3: Schematic arrangement of in-situ utilization of pyro-gas in a batch scale pyrolysis system.

In addition, an electrical heater was provided outside the reactor and a controller unit was used for maintaining the required temperature. Also, a stirrer was fitted appropriately inside reactor for uniform mixing of pellets during pyrolysis reaction. A N_2 cylinder equipped with a regulator was connected with the pyrolysis assembly to ensure inert (N_2) atmosphere inside the reactor. A double pipe heat exchanger was used as a primary condenser for condensing the generated pyro-gas. Inside the condenser, chilled water (~10°C) was circulated to keep the temperature minimum for condensation purpose. During each batch, 0.5 kg of pellet was feed into the reactor unit. Different operating parameters: heating rate (~40°C/min), N_2 flow rate (100 ml/min) and condensing medium temperature (~10°C) were kept constant for all the experiments. All the experimental runs were repeated three times considering same input experimental parameters and conditions to assess the repeatability of the experimental results (Figure 2).

2.4.1 Temperature optimization for GNSP00 to get maximum bio-oil yield.

Initially, 0.5 kg GNSP00 was fed into the reactor to check the feasibility and parameter optimization. Process optimization was done to obtain the maximum bio-oil yield. Except temperature, all other parameters were kept constant in this study. In this regard, experiments were carried out for GNSP00 in the range of slow pyrolysis (400°C to 600°C) (Basu.P Biomass gasification, pyrolysis and torrefaction: Practical design and theory, 2018) with the step size of 50°C. Optimum yield of bio-oil, bio-char and pyro-gas were achived at 550°C; thus it is considered optimum. Hence, at optimized temperature, further experiments were carried out.

2.4.2 In-situ utilization of pyro-gas

Pyro-gas - a potential fuel was not utilized in the previous configurations and combusted openly. Therefore, a holistic approach was developed for complete utilisation of energy obtained from pyro-gas for heating purpose. Since, heat from pyro-gas combustion will lessen the burden imposed on electrical heaters and consequently will lead to energy saving. A standard Bunsen burner was set at the bottom of the pyrolysis reactor (0.5 kg) which uniformly heats the bottom surface as shown in Figure 3. Energy meter connected to the heater of pyrolysis reactor was used during experiment. Energy meter readings were taken in the experiments with and without pyro-gas circulation, and simultaneously percentage saving was calculated.

Percentage of Energy saving was calculated by the ratio of difference of [electricity consumption (kWh) without utilization of pyro-gas] and [electricity consumption (kWh) with utilization of pyro-gas] to [electricity consumption (kWh) without utilization of pyro-gas].

$$\boldsymbol{Energy\ saving}(\%) = \frac{A - B}{A} \quad (1)$$

Pyrolysis of pellets produced from the mixture of processed GNS and crude glycerol were carried out at 550°C for GNSP00 (as discussed in section 2.4.1). The operating conditions and experimental process were same as discussed for GNSP00 (in section 2.4). For each type of pellets four experiments were conducted and average of four set of results were reported. Among four, two experiments were conducted without pyro-gas circulations and two experiments were recorded with pyro-gas circulation.

2.5 Products characterization

Different products obtained at the end of the pyrolysis process like bio-oil, char-pellet, and pyro-gas were analysed in detail.

2.5.1 Char-pellet characterisation

Bio-char pellet produced from pyrolysis process was characterized using proximate analysis, bulk density, durability, calorific value and ultimate analysis. Proximate analysis, bulk density, TGA, ultimate analysis and calorific value of the pellet-char were carried out as per ASTM standard as discussed for loose GNS and GNS pellets (section 2.1, 2.3.2 and 2.3.3). Ultimate analysis (C, H, and N) of pellet-char was carried out using the same instrument as discussed before (section 2.1). Fourier Transform-Infrared (FT-IR) is a spectroscopic method used for identification of the functional group presents in the solid, liquid or a gaseous phase. The spectrum obtained based on the chemical bonds available in the sample. The spectrum represents each wavelength of the light absorbed by specific chemical bonds.

2.5.2 Bio-oil characterisation

Bio-oil obtained from the pyrolysis process was separated in two phases; organic and aqueous phase. Characterisation of bio-oil was carried out using organic phase. From the organic phase of bio-oil the moisture was removed using sodium sulphate (Na_2SO_4) filtration. Then obtained water free bio-oil was used for further analysis. Different properties of bio-oil like pH, density, and calorific value were measured using instrument available at the TCCT Division, SPRERI.

The pH of the bio-oil was measured using a pH meter (pH Tutor, Eutech Instruments, Singapore). Calorific value of bio-oil was measured using an automated bomb calorimeter (IKA® C 5000 Cole-Parmer®, USA). Further characterization of the bio-oil was conducted using FT-IR, Nuclear Magnetic Resonance (NMR, ^1H and ^{13}C, 400 MH_z FT-NMR AVANCE-III, Bruker, USA) and Gas Chromatography-Mass spectrometry (GC-MS, Auto-system XL with Turbo Mass, Perkin Elmer, USA). These analyses were performed at the SICART facility, Vallabh Vidyanagar, Anand, Gujarat, India.

2.5.3 Pyro-gas characterization

The pyro-gas generated during pyrolysis was collected by using a "Gas holder balloon" and afterwards the composition of pyro-gas of pellets was analysed using a Gas Chromatograph (GC) (Sigma Instruments, Vadodara, Gujarat, India) equipped with a Thermal Conductivity Detector (TCD) and two SS packed columns. A molecular sieve column (3 m, 40/50 mesh) was used for the analysis of H_2, O_2, N_2, CH_4 and CO; whereas, a silica gel column (2 m, 80/100 mesh) was used for quantification of CO_2. Column, injector and TCD temperatures were maintained at 140°C, 200°C and 240°C respectively. Argon was used as an inert carrier gas during the GC analysis of the pyro-gas.

3. RESULTS AND DISCUSSION

3.1 Pelletization

Pelletization is an efficient and well-established method to transform the loose biomass into solid biofuel. During experiments crude glycerol was utilized as an additive with processed GNS (ground and sieved GNS) for production of pellets. Proportion of glycerol in the GNS was increased by 20 wt% in a step wise manner. For instance, control 0 wt%, 20 wt%, 40 wt%, 60 wt% and 80 wt% glycerol samples were added into the GNS to densified it. The mixture with 80 wt% crude glycerol was turned out to be slurry; hence maximum amount of crude glycerol in the mixture was limited till 60 wt%.

3.2 Characterization of pellets

All the pellets with different glycerol composition viz. GNSP00 (0 wt% glycerol), GNSP20 (20 wt% glycerol), GNSP40 (40 wt% glycerol) and GNSP60 (60 wt% glycerol) were characterized and compared for proximate analysis, durability, ultimate analysis, calorific value and bulk density. Proximate analysis was carried out for determination of moisture content, ash content, volatile matter and fixed carbon content (by balance) of the pellets. It can be seen thatProximate analysis, Calorific value, bulk density and energy density of pellets were given in Table 1.

For the ash content in GNS pellets similar values were reported by (Kyauta et al., 2015) and (Duan et al., 2014). Due to high volatility of the glycerol, trend obtained for volatile matter is completely reversed than that of trend obtained for ash content. For the volatile matter a similar trend of increasing was reported by (Duan et al., 2014) and (Wibowo et al., 2012).

Major advantage of the pelletization of loose biomass is the increasing energy density. Loose groundnut shell has 2565.66 MJ/m^3 energy density; and it was increased up to ~8686.83 MJ/m^3 after pelletization in the case of GNSP20 (Table 1). Calorific value and bulk density were determined for each type of pellets to determine their energy densities. These were compared with the reported results and these are within the range (Kyauta et al., 2015; Duan et al., 2014; Donev JMKC (2018) Energy Education-Energy density, 2018; Garcia Fernandez et al., 2017; Wibowo et al., 2012; Verma at al., 2012; Lehtikangas, 2001; Lubwama & Yiga, 2017; Serrano et al., 2011; Kluska et al., 2020; Oyelaran et al., 2015; Jamradloedluk & Lertsatitthanakorn, 2015).

Bulk density is highest for the GNSP00 (470.23 kg/m^3), and lowest for the GNSP60 (450.54 kg/m^3). With increasing proportion of glycerol in the mixture, the bulk density of the pellets was decreased; due to lubricating behaviour of the glycerol (Table 1).

Furthermore, the ultimate analysis were also carried out to evaluate the effect of glycerol addition The Carbon (C), Hydrogen (H), Nitrogen (N), Oxygen (O) content, H/C molar ratio and O/C molar ratio in all the pellets were given in Table 2.The Oxygen (O) content was calculated by balance . Durability of the pellets was calculated to determine and compare the strength of the pellets.

All values of ultimate analysis are comparable with the previously reported studies (Bartocci et al., 2018; Duan et al., 2014; Caillat & Vakkilainen, 2013; Wang et al., 2020; Undri et al., 2015; Zhou et al., 2013; Li et al., 2012).

Durability of the pellets decreased as glycerol content increased in the mixture, as crude glycerol is also a lubricant. Due to poor binding property, the durability of the pellets showed decreasing trend with increasing glycerol content in the feedstock (Table 2). Along this line, durability of peanut hull pellets was 90.30% as reported by (Fasina, 2008). Durability of sawdust pellets (100 wt%) along with mixture of sawdust and crude glycerol (sawdust 92.4 wt% + 7.5 wt% glycerol) were reported to be 95.54% and 89.94 % respectively (Demir et al.). Durability of the pellets made from sawdust (100 wt%), and two different mixture of sawdust and glycerol (80 wt% sawdust with 20 wt% crude glycerol and 60 wt% sawdust with 40 wt% crude glycerol) were 95.38%, 80.21% and 75.38% respectively as reported

TABLE 1: Proximate analysis, Calorific value, bulk density and energy density of pellets.

Sr. No.	Material	Proximity analysis (wt%)				Calorific value (MJ/kg)	Bulk density (kg/m^3)	Energy density (MJ/m^3)
		Moisture	Ash	Volatile matter	Fixed carbon			
1	GNSP00	2.33	9.95	72.45	15.27	18.29	470.23	8600.50
2	GNSP20	1.14	7.98	76.09	14.79	18.94	458.65	8686.83
3	GNSP40	2.28	8.23	82.03	7.46	18.69	454.01	8485.44
4	GNSP60	1.85	8.09	85.18	4.88	17.95	450.54	8087.19

TABLE 2: Ultimate analysis and Durability of pellets.

Pellets	C (wt%)	H (wt%)	N (wt%)	O (wt%)	H/C Molar Ratio	O/C Molar Ratio	Durability (%)
GNSP00	43.36	5.86	1.66	49.12	1.0505	0.8504	97.40
GNSP20	45.08	5.06	1.50	48.36	1.2503	0.8053	95.20
GNSP40	40.67	5.97	1.17	52.19	1.6351	0.9633	94.02
GNSP60	39.41	7.14	1.05	52.40	2.0181	0.9975	92.50

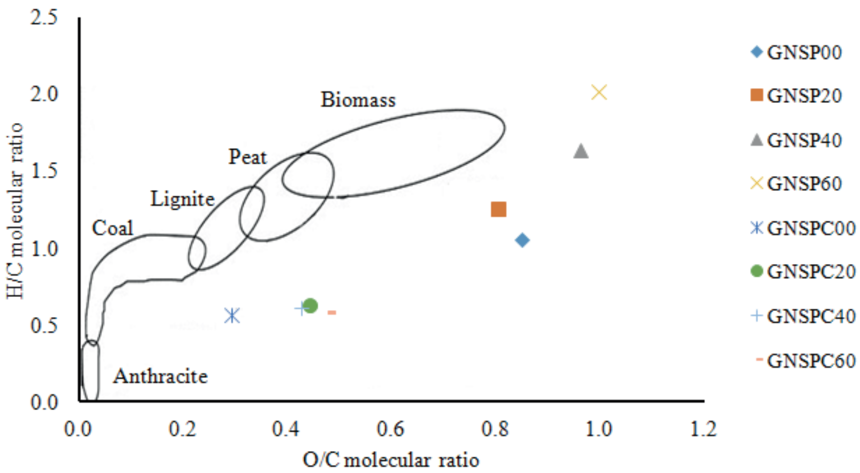

FIGURE 4: Van Krevelen diagram for pellets and pellets bio-char.

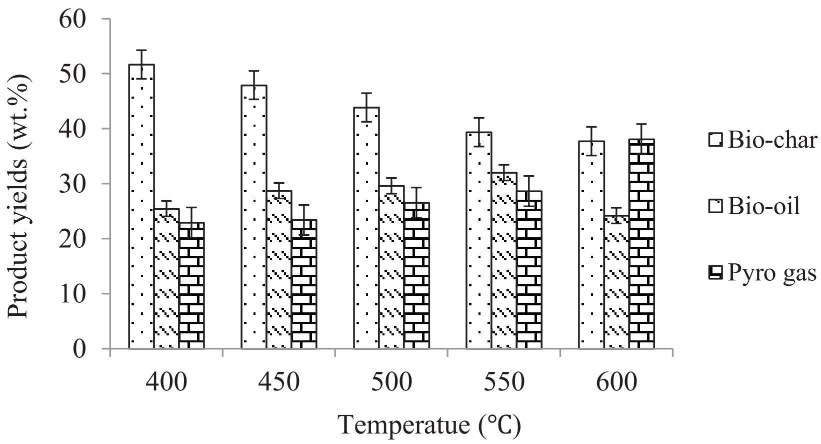

FIGURE 5: Graphical representation of average % yields obtained at different temperature during batch pyrolysis of GNSP00.

by Bartocci et al. (Bartocci et al., 2018). Durability of wood pellets was 98.53% as reported by (Verma at al., 2012).

To make a comparison of quality of pellets with conventional fossil fuels, the Van Krevelen diagram was plotted (Figure 4). Based on the H/C and O/C ratio of all the pellets; it can be seen that all the pellets are falling close to the biomass range.

3.3 Product yields obtained during pyrolysis of pellets

3.3.1 Temperature optimization using GNSP00 to achieve maximum bio-oil yield.

Pyrolysis of GNSP00 was carried out at different temperatures in the range of 400°C-600°C (Figure 5).

From the graph it is observed that with increasing tem-

TABLE 3: Effect of pyro-gas utilization on the electricity consumption for process heating during pyrolysis.

Material	Remarks	Average yield (wt%)			Electricity Consumption (kWh)	Energy Saved (%)
		Bio-char	Bio-oil	Pyro-gas		
GNSP00	WOU	41.6±0.4	31.6±0.5	26.8±0.9	4.1	17.07
	WU	41.2±1	30.4±0.8	28.4±0.15	3.4	
GNSP20	WOU	43.2±0.5	30.8±0.2	26±0.4	4.4	15.09
	WU	40.4±0.5	32.8±0.4	26.8±0.8	3.7	
GNSP40	WOU	40.2±0.8	34.6±0.4	25.2±1.2	4.2	16.66
	WU	39.2±0.7	33.4±0.5	27.4±1.2	3.5	
GNSP60	WOU	30.2±2	40.5±0.25	29.3±1.6	4.4	13.63
	WU	26.8±0.2	41.2±0.1	32±0.3	3.8	

WOU: Without utilization of pyro-gas; WU: With utilization of pyro-gaa

TABLE 4: Proximate analysis bulk density, calorific value, energy density of pellet-char.

Pellets	Proximity Analysis (wt %)				Bulk density (kg/m³)	Calorific value (MJ/kg)	Energy density (MJ/m³)
	Moisture	Ash	Volatile matter	Fixed carbon			
GNSPC00	3.36	21.66	31.16	43.82	376.41	20.89	7863.20
GNSPC20	2.31	28.94	31.17	37.58	339.35	22.51	7638.76
GNSPC40	3.29	27.96	32.85	35.90	326.61	20.48	6688.97
GNSPC60	3.07	29.19	34.75	32.99	272.17	23.67	6442.26

perature, yield of bio-char decreases, while yield of pyro-gas increases. The yield of bio-oil was increased initially and after achieving peak value it starts decreasing. In this study, the maximum bio-oil yield was obtained at 550°C, which was 32.00 wt% for GNSP00 (Figure 5). At the same temperature, bio-char and pyro-gas yields were 39.30 wt% and 28.70 wt% respectively.

3.3.2 Pyrolysis of glycerol containing GNS pellets and in-situ utilization of pyro-gas

All the produced pellets, viz. GNSP00, GNSP20, GNSP40 and GNSP60 were pyrolyzed at 550°C to evaluate the effect of glycerol addition. Bartocci et al. has reported that, the pyro-gas generation is increasing with increasing glycerol proportion in the pellet (Bartocci et al., 2018). In addition, T. Valliyappanet al. has also reported the pyrolysis of raw glycerol and indicated the pyro-gas yield of ~67.6 wt% (Valliyappan et al., 2008). From the inspiring conclusions of above-mentioned articles, we carried-out the in-situ utilization of pyro-gas in the pyrolysis process. Products yield (wt%) along with electricity consumption (kWh) for reactor heating purposes are reported in Table 3.

In this screening, it was observed that during pyrolysis of the GNSP20, GNSP40 and GNSP60 pellets higher amount of bio-oil as well as pyro-gas yield are produced as compared to GNSP00. The highest bio-oil yield was obtained from the GNSP60 (Table 3).

Along with this, the effect of pyro-gas circulation for process heating was also analyzed. Negligible impact of pyro-gas circulation was observed on the yield of products obtained from the pyrolysis (Table 3). The objective of the pyro-gas utilization was to reduce the electricity consumption for reactor heating during the process. Average 15.62% electricity was saved during the whole process. Even though, the maximum pyro-gas yield was obtained from GNSP60, the maximum energy saving was observed in for GNSP00; i.e. 17.07%. It indicates that, the composition of pyro-gas also plays a vital role in the heat generation process via combustion of it.

3.4 Product characterization

3.4.1 Pellet-char characterization

Proximate analysis, bulk density, calorific value, energy density and ultimate analysis

From the proximate analysis result, moisture, ash, volatile matter and fixed carbon content in GNSPC00, GNSPC20, GNSPC40 and GNSPC60 are presented in Table 4. Fixed carbon was calculated by balance.

The bulk density, calorific value and, energy density of GNSPC00 GNSPC20, GNSPC40 and GNSPC60 are given in Table 4.

In this context, bio-char obtained from the pyrolysis of wood pellets have calorific value 30.1 MJ/kg as reported by Yang et al. (Yang et al., 2017). Bio-char obtained from the pyrolysis of GNS have calorific value of 24.21 MJ/kg (Kyauta et al., 2015). Bio-char obtained from the pyrolysis of sawdust have calorific value 23.90 MJ/kg (Soni & Karmee, 2020).

The ultimate analysis result indicates that the C wt%, H wt%, N wt% and O wt% content and H/C and O/C molar ratio in GNSPC00 were found to be 68.3, 3.44, 1.48 and 26.71 and 0.5604 and 0.2932; while in GNSPC20 these components were 59.10, 3.31, 2.52 and 35.07 and 0.6238 and 0.4454; while GNSPC40 these components were 60.32, 3.03, 2.18 and 34.47 and 0.6099 and 0.4289; while in GNSPC60 these components were 58.04, 3.03, 1.89 and 37.04 and 0.5815 and 0.4790 respectively.

Bio-char obtained from the pyrolysis of wood pellets contain C (75.60 wt%), H (3.38 wt%), N (0.22 wt%) and O (10.20 wt%) respectively (Yang et al., 2017). For pellet char Van Krevelen diagram is plotted (Figure 4); to see

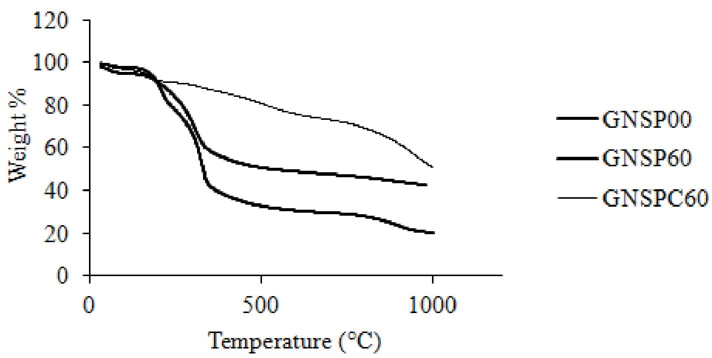

FIGURE 6: TGA analysis of pellets.

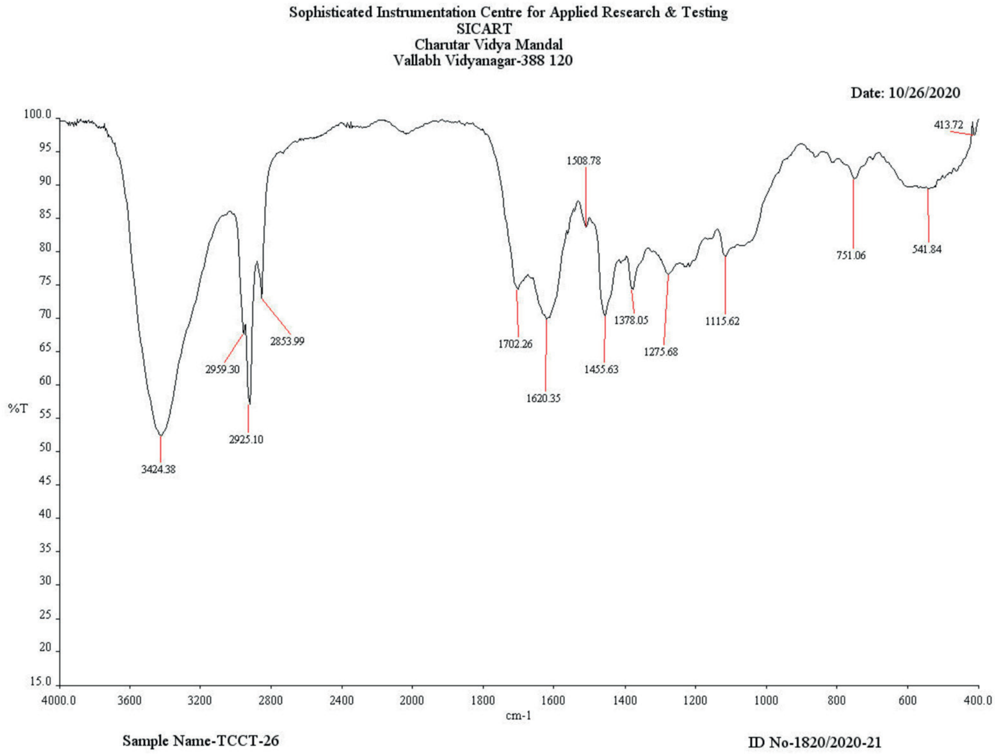

FIGURE 7: FT-IR spectrum of bio-char.

the quality improvement with the help of pyrolysis. Along with this, a comparison with conventional fuel is performed.

TGA Analysis (Mass Loss analysis)

TGA analysis was carried out to determine the thermal behaviour of material. From the TGA analysis, it was noted that up-to 67 wt% GNSP60 and 50 wt% GNSP00 were degraded till 500°C whereas GNSP60 bio-char was only 20 wt% degraded till 500°C. TGA profile of GNSP00, GNSP60 and GNSP60 bio-char is presented in Figure 6.

FT-IR analysis of bio-char

Bio-char was analyzed by FT-IR (Figure 7). The functional groups present are C-I, C-H, C-O, C = C, N-O, C=O and O-H, these groups indicate the different classes of the organic compound like halides, phenols, alkenes, alcohols and aromatics, in bio-char generated from GNSP60. Similar

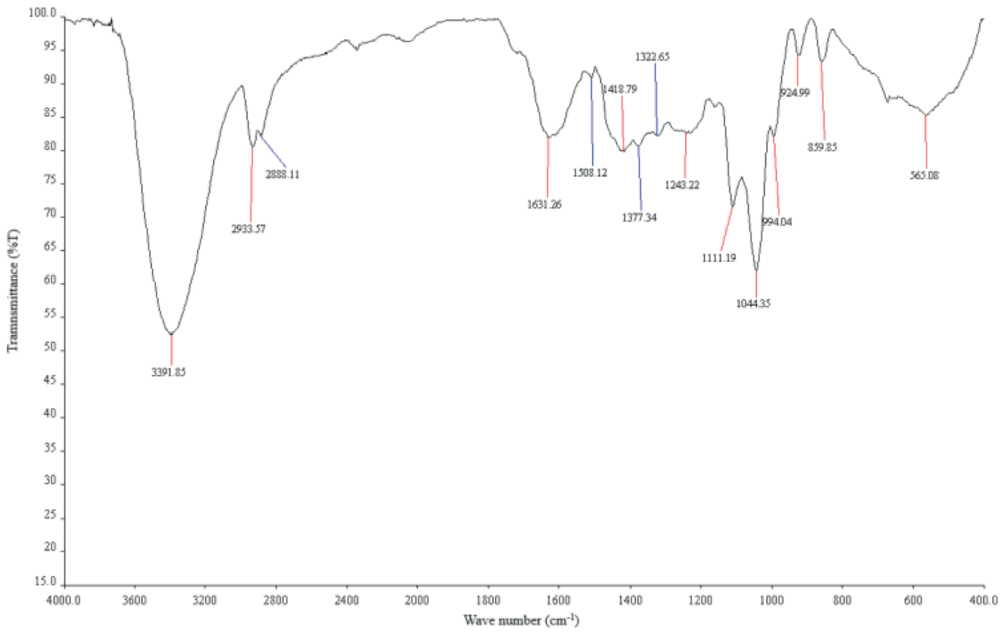

FIGURE 8: FT-IR spectrum of bio-char.

groups were reported in bio-char generated from sawdust and groundnut shell (Undri et al., 2015; Valliyappan et al., 2008; Soni & Karmee, 2020).

3.4.2 Bio-oil characterization

Density, Calorific value and pH

Physical properties of bio-oil like density, calorific value and pH were determined for the bio-oil obtained from GNSP60 at 550°C are 1097.99 (kg/m3), 32.66 (MJ/kg) and 4.6 respectively.

The calorific value of the bio-oil is comparable with methanol (23 MJ/kg), ethanol (29.7 MJ/kg) and dimethyl ether (31.7 MJ/kg) and suggests its suitability for the thermal applications. The calorific value, pH and density of bio-oil obtained from pyrolysis of sawdust were 28.57 MJ/kg, 4.3 and 1253 kg/m^3 (Soni & Karmee, 2020) The bio-oil

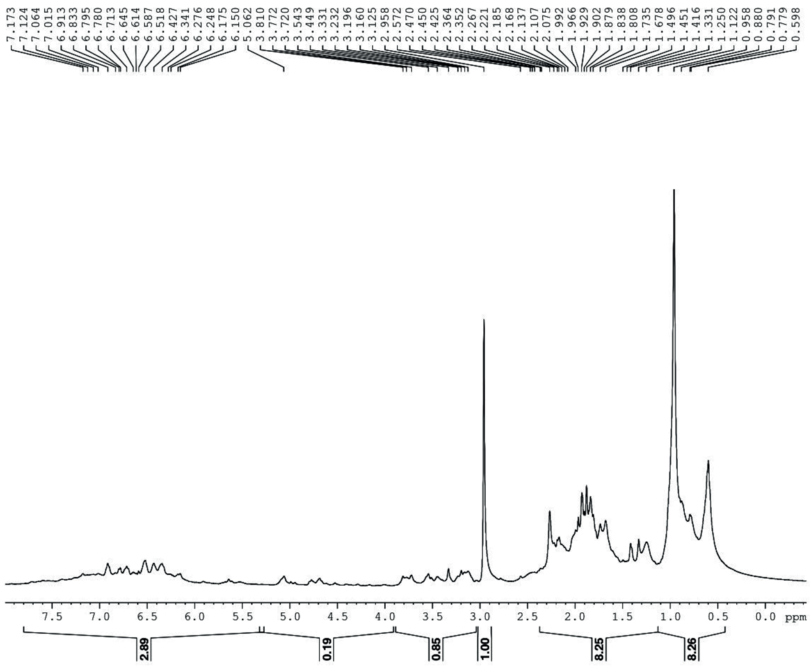

FIGURE 9: H NMR spectrum of bio-oil.

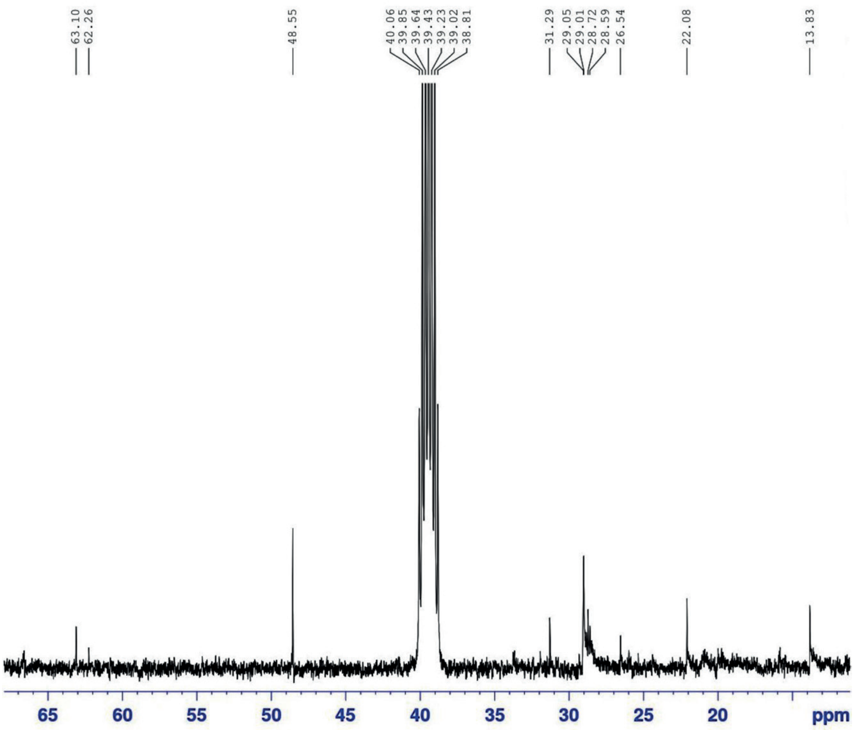

FIGURE 10: C NMR spectrum of bio-oil.

obtained from pyrolysis of wood pellets have calorific value 24.2 MJ/kg (Yang et al., 2014). The calorific value of bio-oil obtained from pyrolysis of groundnut shell was 24.22 MJ/kg (Tinwala et al., 2015).

FT-IR analysis of bio-oil

The obtained spectrum shows the presence of major functional groups namely, C-Br, C=C, C-H, C-Cl, C-N, O-H, N-O and C=O in the bio-oil (Figure 8).

Absorbance peaks in range 2840-3000 cm^{-1} suggest the C-H bonds. The absorbance peak at 3385 cm^{-1} and 1364 cm^{-1} suggest the O-H bonds. The absorbance peak like 1461 cm^{-1} and 756 cm^{-1} indicate the availability of alkane and alkene bonds. The peaks at 1674 cm^{-1}, 790 cm^{-1}, 715 cm^{-1} and 885-980 cm^{-1} indicate C=C bonds in the bio-oil. The peaks range of 1500-1600 cm^{-1} is an indication of N-O bonds. The peak in the range of 1020-1350 cm^{-1} is because of the nitrogen containing substance present in the bio-oil (Lingegowda et al, 2012). The spectrum show different classes of organic compounds such as phenols, aliphatic alcohols, alkenes, ketones, nitrogen, aldehydes, halides, carboxylic acids and nitrogen containing compounds (Undri et al., 2015; Soni & Karmee, 2020; Radhakrishnan & Gnanamoorthi, 2015).

^{1}H and ^{13}C NMR analysis

^{1}H and ^{13}C NMR analyses are used for structural determination of chemical compounds. ^{1}H NMR gives an indication about environment of protons; and ^{13}C NMR for the environment of carbon present in the chemical compounds. ^{1}H NMR shows the presence of alkyl, aryl, allylic, ketone and alcohol based compounds in bio-oil and ^{13}C NMR show the presence of alkyl, aromatic, alkenes, carboxylic acids, ester and alcohol containing compounds in the bio-oil (Undri et al., 2015; Soni & Karmee, 2020). The ^{1}H NMR and ^{13}C NMR of biooil are presented in Figure 9 and Figure 10.

GC-MS analysis

Bio-oil generated from the pyrolysis process contain complex mixture of chemical compounds. GC-MS is one of the accurate techniques for determination of the lower molecular weight compounds available in the bio-oil sample. During GC analysis of the bio-oil different chemical compounds like phenols, ketones, alcohols, nitrogen containing compounds, aldehydes, halides, and carboxylic acids were found. (Undri et al., 2015; Soni & Karmee, 2020; Radhakrishnan & Gnanamoorthi, 2015).

3.5 Pyro-gas characterization

Gas-chromatography analysis of generated pyro-gas was carried out. Hydrogen (H_2) vol. %, Oxygen (O_2) vol. %, Nitrogen (N_2) vol. %, Methane (CH_4) vol. %, Carbon monoxide (CO) vol. %,, Carbon dioxide (CO_2) vol. %, was detected in the pyro-gas while Carbon dioxide (CO_2) was calculated by balance.

Hydrogen (H_2), Oxygen (O_2), Nitrogen (N_2), Methane (CH_4), Carbon monoxide (CO), Carbon dioxide (CO_2) were found in GNSP00 were 0.72 vol. %, 3.85 vol. %, 16.22 vol. %, 32.26 vol. % and 41.67 vol. %; while in GNSP20 the components are 4.38 vol. %, 1.31 vol. %, 13.34 vol. %, 12.71 vol. %, 34.75 vol. % and 33.51vol. %; while in GNSP40 the components are 10.23 vol. %, 2.06 vol. %, 11.22 vol. %, 11.83 vol. %, 24.23 vol. % and 40.43 vol. % ;while in GNSP60 the components are 6.00 vol. %, 5.69 vol. %, 26.44 vol. %, 5.55 vol. % and 28.24 vol. %.

The calorific values of the pyro-gases obtained from GNSP00, GNSP20, GNSP40 and GNSP60 are 6.03 MJ/m^3, 9.40 MJ/m^3, 8.39 MJ/m^3, 8.39 MJ/m^3 and 6.19 MJ/m^3 respectively.

Pyrolysis of wood pellets at 450°C generated pyro-gas with composition of H_2 (2.24 vol. %), N_2 (5.54 vol. %), CO (34.70 vol. %), CH_4 (7.2 vol. %), CO_2 (50.27 vol. %) and the calorific value 7.27 MJ/m^3 was reported by Yang et al (2014, 2017). Pyrolysis of sawdust produced pyro-gas with composition : H_2 (1.59 vol. %), O_2 (2.48 vol. %) N_2 (13.61 vol. %), CO (54.23 vol. %), CH_4 (8.02 vol. %) and CO_2 (50.27 vol. %) (Soni & Karmee, 2020).

4. CONCLUSIONS

In this study, co-pelletization of GNS with crude glycerol was performed and efforts were made towards using energy in crude glycerol. Pelletization was carried out which resulted in increasing energy density of crude glycerol containing pellets compared to GNS pellets. Characterisation of pellets showed the rise in volatile matter from 72.45 wt% to 85.18 wt% with rise in crude glycerol proportion.

In addition, pyrolysis was carried out in a batch scale. Energy rich pyro-gas was used for heating of pyrolysis reactor in an in-situ manner and shows maximum 17% electrical energy saving. Bio-oil yield increased from 30 wt% to 41 wt% and also pyro-gas yield increased from 28 wt% to 32 wt% with increase in glycerol content in pellets. Characterisation of pyrolysis products revealed that calorific value of pellet-char was found to be 23.67 MJ/kg and bio-oil was 32.66 MJ/kg. The obtained bio-oil can be used as a fuel and also as a feedstock in chemical industries.

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