



KINETIC PARAMETERS OF TORREFACTION PROCESS OF ALTERNATIVE FUEL PRODUCED FROM MUNICIPAL SOLID WASTE AND CHARACTERISTIC OF CARBONIZED REFUSE DERIVED FUEL

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ABSTRACT

Torrefaction is next to drying, pelletizing and briquetting one of the methods for pre-treatment of fuels for later use for energy purposes. Torrefaction is a thermo-chemical process, carried out in the temperature range from 200 to 300°C, under atmospheric pressure and inert gas environment. The study involved a refuse derived fuel (RDF) produced from municipal solid waste in a mechanical-biological plant. The aim of this work was to determine the kinetic parameters of the torrefaction process of RDF and to examine the effect of temperature and the residence time on fuel properties of biochar. Torrefaction process was carried out in the temperature range from 200 to 300°C with the temperature interval of 20°C. The residence was respectively 20, 40 and 60 minutes for each temperature. RDF and the resulting carbonized refuse derived fuel (CRDF) have been subjected to the following analysis: moisture content, organic matter, combustible and volatile content, ash content, and higher heating value. The determined activation energy of RDF torrefaction was 3.71 kJ·mol⁻¹. The thermogravimetric analysis indicated that during torrefaction, mostly lingo-cellulosic, and hemi-cellulosic biomass present in RDF decomposes during torrefaction. Studies have shown the influence of residence time and temperature on fuel properties of the obtained CRDF. The highest heating value of the CRDF was obtained for the temperature of 260°C, and residence time 20 minutes.

1. INTRODUCTION

Waste conversion for energy purposes offers an effective way of recycling. This approach is very important in times of increased energy demand and the requirements of waste utilization and recycling. One of the ways to maximize the production of electricity and heat from waste is to produce Refuse Derived Fuel (RDF) and direct it for later thermal recovery and/or recycling.

RDF is a converted waste material that is generated by mechanical treatment (grinding, sorting) of combustible municipal and industrial wastes, including primarily plastics, paper and wood. RDF is most often used for the production of electricity and heat (Dalai et al., 2009; Preston and Kollberg 2016).

In Poland, municipal wastes are sent first to the Regional Municipal Waste Treatment Plant or to a waste incineration plant. At the Regional Municipal Waste Treatment Plant waste is subjected to mechanical biological treatment. The waste stream in the plant is divided into two fractions using a sieve with a mesh size of 80 mm. From the over-sieve fraction, materials that can be recycled are selected, and then unselected waste is converted into alternative fuel (RDF) for a waste incineration plant or cement plant. The under-sieve fraction undergoes a biostabilization process. After this process, the obtained stabilized waste is sieved on a 20 mm sieve. The obtained over-sieve fraction is most often disposed at the landfill, and the fine fraction is used as a material for landfill covering (Pietryszyn and Primus 2015, SPC report 2015, Kinitz 2014).

At present, there are 127 Regional Municipal Waste Treatment Facilities in Poland, and their total capacity is 8164 thousand Mg per year. RDF incineration plants can be divided into two types: cement plants and waste incineration plants. 9 cement plants in Poland have the total capacity of 1200 thousand Mg of RDF per year. In Poland, waste incinerators are currently in the initial stages of com-



Detritus / Volume 03 - 2018 / pages 75-83 https://doi.org/10.31025/2611-4135/2018.13702 © 2018 Cisa Publisher. Open access article under CC BY-NC-ND license missioning or in the final phase of construction. Ultimately, 7 incineration plants will operate in the area of Poland, with a total capacity of 1 014 thousand Mg per year (Pietryszun and Primus, 2015).

The total mass of the produced RDF amounts 2 million Mg per year. The RDF produced in Poland is characterized by the following properties: moisture content fluctuates from 3.20% to 24.80%, ash content from 11.00 to 24.30% d.m., sulphur content from 0.12% to 0.76% d.m.. Higher Heating Value (HHV) ranges from 15.80 to 23.08 MJ·kg⁻¹, is Low Heating Value (LHV) from 14.53 to 21.59 MJ·kg⁻¹. The RDF is also characterized by high heterogeneity, which adversely affects the possibility of maintaining constant fuel properties (Ahn et al., 2013; Nowak and Szul, 2016).

RDFs are used for energy and heat production in cement plants and waste incineration plants with a total capacity of 1.996 thousand Mg per year (Krawczyk and Szczygieł 2013; Kinitz N., 2014). It should be noted that the total capacity of RDF utilization installations is two times smaller than the estimated annual volume of RDF produced. This situation results in a decrease in costs for wastes utilization in a thermal processing plant and increase in the requirements for the quality of RDF produced by the MBPs. At present, the essential parameters to be met by RDF are: calorific value >20 MJ·kg⁻¹, moisture content <15%, heavy metal content <2500 mg/kg, chlorine content <1%, sulphur content <1.5%, and ash <15%. In addition, the RDF should have a granularity of less than 40 mm and be a homogeneous mixture (Hryb and Biegańska, 2013).

Torrefaction also called roasting, high-temperature drying, low-temperature pyrolysis could be a helpful solution for overcoming problems with RDF qualitative requirements. Torrefaction is a thermo-chemical process, with following characteristics: temperature 200-300°C, heating rate <50°C·min⁻¹, residence time <60 minutes, no oxygen, atmospheric pressure (Tumuluru et al., 2011). Five process phases can be distinguished: pre-heat, pre-drying, drying and transient heating, torrefaction, cooling of the product (Bergman et al., 2005). As a result of the process, two products are obtained: biochar and torrefaction gas one with a mass balance of 70-80% and 23-30% respectively. The solid product is called biocarbon when agricultural or forestry biomass is used as a substrate. For other substrates, it is called carbonate or biochar (Malińska, 2015). The gas product is referred to as a tor-gas (Bergman et al., 2005).

The solid product resulting from the processing of agricultural or forestry biomass is characterized by:

- High energy density. Processed biomass contains 70-80% of the initial mass and 80-90% of initial energy (Tumuluru et al., 2010);
- Decrease in moisture content. After the torrefaction process, the moisture content of the obtained product is approximately 1-2% mass (Tumuluru et al., 2010);
- Hydrophobic properties. Processed biomass manifests high hydrophobicity. Maximum water uptake is 1-6% (Tumuluru et al., 2010) (e.g. water content in unprocessed wood biomass ranges from 12 to 22%, bark from 45 to 55% (Kordylewski et al., 2008));
- Increased carbon content. The concentration of carbon

in the structure of the compound results in increased biocarbon reduction properties (Bergman, 2005);

- Reduction of oxygen and hydrogen. The O/C and H/C ratios are reduced, resulting in an increase in the attractiveness of biocarbon as a substrate for the gasification process (Prins, 2005);
- Better milling properties. Due to the depolymerisation of cellulose fibres, lignin and hemicellulose biochar grinding requires less energy since the structure and form of the particulate matter is similar to carbon (Bergman et al., 2004).

Due to the above, torrefaction process may be a good way to increase the fuel properties of RDF. However, this process has not been characterized or understood deeply. This paper presents the characteristics of the thermal decomposition of RDF using thermogravimetric analysis (TGA). Using the qualitative interpretation method of the TGA curve, changes in the mass decrease pattern of the sample under linear temperature increase were observed, whereby a comparison of the mass drop within temperature range with the values given in literature of the individual RDF components was conducted. The quantitative interpretation of kinetic parameters such as the reaction rate constant and activation energy. These parameters are indispensable in the torrefaction modelling process.

RDF and produced carbonates are characterized in terms of fuel properties. The conducted analysis allowed to determine the suitability of the torrefaction as an alternative fuels valorisation process.

2. MATERIAL AND METHOD

2.1 RDF used in the study

The RDF used in the study was taken from a mechanical-biological waste treatment facility with the status of a regional waste treatment plant. The facility is located in the village of Gać, Poland (in the region of Lower Silesia). The process of production RDF from municipal solid waste is presented in Figure 1.

A general 250 kg sample was taken from RDF's production line and then a laboratory sample of 5 kg was separated from the general sample by quartering (PN-Z-15006:1993). In order to homogenize the material (RDF and RDFs), it was ground to particle size ≤ 0.425 mm with the use of the LMN 100 knife mill. The material to be tested was prepared in the way presented below.

2.2 Carbonized Refuse Derived Fuel production method

The biochar, previously referred to as Carbonized Refuse Derived Fuel (CRDF) (Białowiec et al., 2017) was obtained by means of the SNOL 8.1/1100 muffle furnace (Figure 2). CRDF samples were generated under the following conditions:

- Temperature range from 200 to 300°C (temperature interval of 20°C);
- Retention time: 20, 40, 60 minutes for each temperature;



FIGURE 1: The configuration of RDF production lines at MBT plant in Gać.



FIGURE 2: Schematic figure of the experimental set-up of CRDF generation.

- Temperature rise: 50°C·min⁻¹ (maximum heating rate);
- Used gas: carbon dioxide;
- Gas flow: 10 dm³·h⁻¹.

The heating of the reactor was commenced 5 minutes after gas introduction into the device began. Carbon dioxide was cut off when the temperature inside the reactor during the cooling phase reached 100°C (Madanayake et al., 2016).

2.3 Physical and chemical analysis of RDF and CRDF

The RDF and generated CRDF from torrefaction were tested for:

- Morphological composition (only RDF) in accordance with Malinowski and Wolny-Koładka (2012);
- Moisture content by means of the KBC65W laboratory dryer in accordance with the PN-EN 14346:2011 stan-

dard;

- Content of organic matter by means of the SNOL 8.1/1100 muffle furnace in accordance with the PN-EN 15169:2011 standard;
- Combustible and non-combustible content by means of the SNOL 8.1/1100 muffle furnace in accordance with the PN-Z-15008-04:1993 standard;
- Volatile content by means of the SNOL 8.1/1100 muffle furnace in accordance with the PN-G-04516:1998 standard;
- Higher heating value by means of the IKA C2000 Basic calorimeter in accordance with the PN-G-04513:1981 standard.

Each of the designations was repeated 3 times.

2.4 Thermogravimetric analysis (TGA) of RDF

The thermogravimetric analysis was carried out by means of the Czylok RST 40.200/110P stand-mounted tubular furnace (Figure 3).

The study used the method of qualitative and quantitative interpolation of the TGA curve. The qualitative method allows for determining the mass deviations of the sample to be tested at a set temperature. By this analysis, the distribution of particular chemical compounds that build up the sample may be observed. A quantitative method allows for determining the kinetic parameters of the process. The measurement is based on accurate determination of the mass change and its rate at particular temperatures.

The first method was carried out under the following conditions:

- Temperature from 10 to 850°C;
- Temperature rise: 10°C·min⁻¹ (maximum heating rate);
- Used gas: carbon dioxide;
- Gas flow: 10 dm³·h⁻¹.

The second method was carried out under the follow-



FIGURE 3: Reactor set-up: 1 - a vessel filled with solid fuel sample, 2 - electrically heated reactor, 3 - electronic balance, 4 - electric power feeder (regulator), 5 - rotameter, 6 - bottle with carbon dioxide, 7 - gaseous products of pyrolysis/torrefaction process, 8 - temperature indicator, 9 - thermocouple, 10 - exhaust chimney.

ing conditions:

- Temperature range from 200 to 300°C (temperature interval of 20°C);
- Retention time: 60 minutes for each temperature;
- Used gas: carbon dioxide;
- Gas flow: 10 dm³·h⁻¹.

Based on TGA results, the reaction rate and activation energy within the torrefaction temperature range was calculated by Statistica 13.1 software. The reaction constant rate of the thermal transformation of the material was calculated on the basis of a first-order reaction (Eq. 1, Eq. 2) (Bates et al., 2012):

$$M_s = M_s^0 \cdot e^{-k \cdot t} \tag{1}$$

$$\ln \frac{M_s^0}{M_s} = k \cdot t \tag{2}$$

where: M_s^0 is initial mass, g, M_s is mass per unit, g, k is reaction rate constant, 1·s⁻¹, t is time, s.

The Arrhenius equation (Eq. 3) (Bates et al., 2012) represents the dependence of the reaction constant rate k on the temperature T:

$$k(T) = A \cdot \exp{-\frac{E_a}{R \cdot T}}$$
(3)

The logarithmic form of the equation (Eq. 3) is shown below:

$$\ln k(T) = \ln A - \frac{E_a}{R \cdot T} \tag{4}$$

where: *R* is universal gas constant, 8.314 J·(mol·K)⁻¹, *T* is temperature, K, *A* is a pre-exponential factor, $1 \cdot s^{-1}$, E_a is activation energy, J·mol-1, *k* is reaction constant rate, $1 \cdot s^{-1}$.

Using the Arrhenius equation, activation energy can be calculated by means of the reaction constant rate. Ln(k) is a linear function of 1·T-1 (Eq. 5) (Soria-Verdugo, 2015).

$$y = a \cdot x + b \tag{5}$$

where: $y = \ln(k)$, $b = \ln A$, $a = \frac{E_a}{R}$, $x = 1 \cdot T$.

3. RESULTS AND DISCUSSION

3.1 Results of the physical and chemical analysis of the substrate

RDF morphological composition is shown in Table 1.

The percentage share of highly calorific waste (plastics, paper, wood, textiles) was 54.3%. This value is low, but lies within the lower range of values given in literature, where the proportion of highly calorific waste was from 53.2% to 100% (Seo i in. 2010; Miskolczi i in., 2011; Kara, 2012; Kruger i in., 2014; Akdag i in., 2016; Çepolioğullar Ö i in., 2016).

The average results of the physical and chemical analyses of RDF are presented in Table 2.

Moisture content in the RDF was 17.31%. This value is within the upper limit of the moisture content in RDF. The

TABLE 1: The	average	morphological	composition	(N=3)	of	the
analysed RDF.						

Waste group	Share of a waste group (%)
Plastics	30.3
Paper	11.3
Wood	10.5
Composite waste	8.3
Rubber	5.6
Textiles	2.2
Metal	0.1
Glass	0.1
Kitchen and garden waste	0.1
Other unidentified waste and mineral waste	31.6

TABLE 2: The average (±SD - standard deviation) values of physical and chemical properties of the analysed alternative fuel.

Sample	Alternative fuel
Moisture (%)	17.31 ± 4.48
Organic matter content (%)	85.80 ± 15.32
Volatile content (%)	85.13 ± 1.04
Combustible content (%)	86.75 ± 1.82
Ash (%)	13.25 ± 1.82
High calorific value (MJ·kg ⁻¹)	25.41 ± 1.58

moisture content reported in the literature ranges from 1.6% to 17.4% (Akdag et al., 2016; Edo et al., 2016; Manya et al., 2015; Seo et al., 2010; Singh et al., 2011).

Analysing the results of the content of organic matter and the content of combustible components, it must be noted that RDF is mostly built of organic materials that break down to 550°C. This is reflected in the morphological composition of the alternative fuel, which consists mainly of materials (plastics and wood) that undergo decomposition at temperatures of 550°C (Robinson et al., 2016). The residual matter is ash, whose average value in the analysed material was 13.25%. The ash content in RDF ranges from 8.64% to 26.29% (Ahn et al., 2013; Akdag et al., 2015; Çepolioğullar et al., 2016; Miskolczi et al., 2011; Seo et al., 2010; Singh et al., 2012).

The determined high calorific value was higher than usually given in the literature - from 17 to 22 $MJ \cdot kg^{-1}$ (Akdag et al., 2016; Çepolioğullar Ö et al., 2016; Whyte et al., 2015).

3.2 Results of a thermogravimetric analysis

During the thermogravimetric analysis, two weight drops were observed. The mass decreases occurred between 210°C and 380°C, and between 380°C and 730°C. Material transformation followed one by one (Figure 4).

The first thermal decomposition may be linked of hemicellulose and cellulose breakdown. The temperature ranges of the thermal decomposition of these two compounds are as follows: hemi-cellulose 220-315°C, cellulose 315-370°C (Akdeg et al. 2016; Carrier et al., 2011; Lu et al., 2012). The second peak may be linked to the decomposition of plastics. Degradation of these materials begins above 400°C (Robinson et al., 2016; Sanchez-Silva et al., 2012; Stępień et al., 2017).

An equation (1) was used to calculate reaction constant rates and activation energies for temperatures within the range of 200-300°C (Table 3).

The estimated activation energy was 3.71 kJ·mol⁻¹. Literature review showed that activation energy for RDF depends on temperature ranges: between 240-380°C and between 250-370°C. The values obtained by Singh et al. (2012) and Grammelis et al. (2007) were much higher and were 97.8 and 121 kJ·mol⁻¹, respectively.

3.3 Results of the physical and chemical analysis of the CRDF

The average results of the physical and chemical analyses of carbonized refuse derived fuel are presented on 3D



FIGURE 4: DTG and TGA characteristics of RDF.

charts with spline interpolation (Figures 5-10).

Moisture content for untreated RDF was 17.31%. The residual water content in carbonates was the smallest at temperature 200°C and retention time 20 minutes. In that case, the moisture decreased to 0.13% (Figure 5). The moisture content increased to 1.27% along with the increase of the temperature and retention time of the torrefaction process. The studies conducted by Nobre et al., (2016), found that the torrefaction process had a positive effect on the moisture content reduction. They indicated that the content of water 6.02% in the raw material dropped to 2.23% during torrefaction at 300°C for 30 minutes.

The contents of organic matter (Figure 6), combustible (Figure 7) and volatile components (Figure 8) were similar. This was correlated with characteristics of thermal decomposition of materials present in RDF, including plastic and lingo-cellulosic compounds. These materials undergo thermal degradation of up to 550°C. The higher content of combustible components in relation to the organic matter is associated with a high temperature distribution of volatiles (Lu et al., 2012, Robinson et al., 2016). The content of organic matter, combustible and volatile components in relation to unprocessed biomass was reduced by 6%, 7%, and 7%, respectively. These values are low compared to the results obtained by Nobre et al. (2016), where the decrease in the volatiles amounted to 22% at 300°C torrefaction with 30 minutes residence time. Such a large difference may be due to the different morphological composition of the tested samples. The highest residual organic matter has been found for temperature range from 240 to 260°C, and residence time 40 minutes (Figure 6). The tendency of combustibles content decrease with the increase in torrefaction temperature, for all tested residence times, was observed (Figure 7). A similar relationship was found for volatiles content, with the highest value for a variant with temperature 200°C, and 60 minute of residence time (Figure 8).

The ash content in CRDF is indirectly related to the increase in temperature and residence time that affects the sample gasification. It should be noted that ash content in carbonate increased to over 23% (Figure 9). The raw material was characterized by the ash content of 13%. The maximum ash content in torrefied materials was lower compared to RDF. The maximum value of the quoted parameter can be as high as 26%.

The decrease in HHV is related to the ash content increase and the gasification of the volatile component. According to the principles of torrefaction, the substrate

should have a low content of inert parts, because after the process, when partial degassing of the volatiles occurs, the mass ratio of the ash to the entire mass of the particle increases (Tumuluru et al., 2011). In the case of RDF torrefaction, the optimum value of the process was 260°C with 20 minutes of residence time. For this torrefaction parameters, the average value of HHV was 26.22 $MJ\cdot kg^{-1}$. Comparing this value with the average HHV of unprocessed material, the obtained value was higher by 0.81 $MJ\cdot kg^{-1}$.

The observed tendency of HHV decrease along with the increase in temperature and retention time was also reflected in the research carried out by Nobre et al. (2016), in which the HHV heat decreased from 17.68 to 15.70 $MJ\cdot kg^{-1}$.

Due to the low content of lingo-cellulosic compounds in the waste, they could have reacted completely at a temperature lower than 300°C. The main component of RDF were plastics, whose distribution starts at 400°C (Robinson et al., 2016). The complete conversion of the lignocellulose parts caused a rise in the ash content, which had an impact on the ash presence in the sample. The final effect was that the higher ash content resulted in the decrease in HHV.

Table 4 shows the comparison of raw material with the obtained CRDF's.

4. CONCLUSIONS

The TGA analysis has shown that one of the materials groups contained in RDF is decomposing within the temperature range of the torrefaction process. The observed transformation was attributed to the decomposition of cellulose and hemicellulose which build wood and paper in RDF. The calculated activation energy in the temperature range of 200 to 300°C was 3.71 kJ·mol⁻¹.

The torrefaction process has a positive effect on reducing the moisture content. Moisture decreased from 17% to 1%.

As the temperature and retention of the torrefaction process increased, the material degassed significantly, resulting in an increase in ash content in the product. This parameter unfavourably influences the HHV.

The highest HHV of CRDF was achieved for temperature 260°C, and residence time 20 minutes.

Scientific research on the torrefaction of RDF is still at an early stage and needs to be further developed in order to accurately characterize the process and the obtained products.

R ²	E, J∙mol⁻¹	ln(k), 1·s⁻¹	1·T ⁻¹	R ²	k, 1·s⁻¹	Т, К
	3.71E+03	-1.12E+01	2.11E-03	0.89	1.41E-05	473
		-1.11E+01	2.03E-03	0.77	1.44E-05	493
0.55		-1.11E+01	1.95E-03	0.78	1.47E-05	513
		-1.12E+01	1.88E-03	0.78	1.37E-05	533
		-1.10E+01	1.81E-03	0.80	1.66E-05	553
		-1.10E+01	1.75E-03	0.67	1.66E-05	573

TABLE 3: Reaction constant rate and activation energy.



FIGURE 5: Effect of torrefaction temperature and retention time on the moisture content in CRDF.



FIGURE 7: Effect of torrefaction temperature and retention time on the combustible content in CRDF.



FIGURE 9: Effect of torrefaction temperature and retention time on the ash content of CRDF.



FIGURE 6: Effect of torrefaction temperature and retention time on the organic matter content in CRDF.



FIGURE 8: Effect of temperature and retention time on the volatile content in CRDF.



FIGURE 10: Effect of torrefaction temperature and retention time on the HHV of CRDF.

TABLE 4: The average (±SD - standard deviation)) values of physical and chemical properties o	of the analysed alternative fuel and CRDF's.
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·		Moisture (%)	Organic matter content (%)	Volatile content (%)	Combustible content (%)	Ash (%)	High calorific value (MJ·kg ⁻¹)
		17.31 ± 4.48	85.80 ± 15.32	85.13 ± 1.04	86.75 ± 1.82	13.25 ± 1.82	25.41 ± 1.58
	20	0.08 ± 0.07	79.33 ± 0.30	79.29 ± 0.38	81.95 ± 0.30	18.04 ± 0.30	24.94 ± 0.31
200	40	0.94 ±0.07	80.05 ± 0.89	77.50 ± 0.57	81.34 ± 1.00	18.65 ± 1.00	22.18 ± 0.49
	60	0.76 ± 0.10	80.83 ± 0.61	82.01 ± 0.85	82.65 ± 0.47	17.34 ± 0.47	25.15 ± 0.03
220	20	0.54 ± 0.05	79.93 ± 0.49	81.65 ± 1.10	81.70 ± 0.47	18.29 ± 0.7	26.53 ± 0.38
	40	1.63 ± 0.77	73.85 ± 0.47	80.60 ± 0.57	80.94 ± 3.08	24.25 ± 11.49	23.50 ± 0.19
	60	0.97 ± 0.03	78.42 ± 0.71	79.90 ± 0.31	79.69 ± 0.70	20.30 ± 0.70	24.64 ± 0.47
240	20	0.26 ± 0.02	77.41 ± 1.13	79.05 ± 0.76	78.85 ± 1.12	21.14 ± 1.12	23.10 ± 0.50
	40	0.80 ± 0.45	92.41 ± 0.85	80.84 ± 0.70	81.49 ± 0.39	19.01 ± 0.51	21.98 ± 0.32
	60	1.27 ± 0.08	76.10 ± 0.35	76.87 ± 0.67	77.82 ± 0.27	22.17 ± 0.27	25.34 ± 0.29
260	20	0.55 ± 0.05	80.45 ± 0.44	80.27 ± 0.44	81.79 ± 0.46	18.20 ± 0.46	26.22 ± 0.84
	40	1.77 ± 0.14	78.86 ± 0.60	80.11 ± 0.27	80.71 ± 0.60	19.28 ± 0.60	24.11 ± 0.31
	60	0.73 ± 0.02	76.55 ± 1.41	78.06 ± 0.88	78.49 ± 1.32	21.50 ± 1.32	22.65 ± 0.38
280	20	0.79 ± 0.01	78.31 ± 0.27	79.98 ± 1.07	80.11 ± 0.28	19.88 ± 0.28	23.74 ± 0.31
	40	0.73 ± 0.04	73.19 ± 0.11	75.13 ± 0.26	75.77 ± 0.14	24.22 ± 0.14	22.91 ± 0.44
	60	0.37 ± 0.06	70.62 ± 0.31	74.09 ± 0.70	73.30 ± 0.28	26.69 ± 0.28	22.26 ± 1.21
300	20	0.25 ± 0.023	74.40 ± 0.19	76.60 ± 0.23	76.38 ± 0.17	23.61 ± 0.17	22.91 ± 0.13
	40	1.23 ± 0.10	75.33 ± 1.06	76.73 ± 1.00	77.29 ± 0.94	22.70 ± 0.94	25.47 ± 0.82
	60	1.08 ± 0.07	76.27 ± 0.59	76.34 ± 1.04	78.52 ± 0.61	21.47 ± 0.61	24.12 ± 0.76

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