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Solubility of Tar Model Compounds in Various Solvents for Tar Removal in a Dual Fluidized Bed Biomass Gasification Process

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Abstract. Production of high quality product gas via biomass steam gasification is a promising technology. However, impurities in the product gas, namely tars, cause problems in the downstream gas processing operations and thus they need to be removed efficiently. Oil scrubbing is an effective solution for tar removal due to its non-polar characteristic which is similar to tar nature. In this research, solubility values of five simulated tar compounds were experimentally investigated for selecting the new scrubbing solvent. The simulated tar compounds investigated represent those found in the dual fluidized bed steam gasification of wood biomass, which are: naphthalene, biphenyl, anthracene, fluoranthene, and pyrene. The scrubbing solvents tested in this research are classified into biodiesels, vegetable oils, and diesel. Biodiesel used are rapeseed methyl ester (RME) and 2 different palm methyl esters (denoted as PME1 and PME2). Vegetable oils are sunflower oil, refined palm oil, Thai rice bran oil, and crude palm oil. All of the solubility tests were performed in the laboratory-scale test-rig at 30, 50, 70, and 80°C. Biodiesels are found to be the effective solvent in dissolving the tar compounds. PME1 shows the similar tar removal performance to RME but is more readily available; therefore, PME1 is chosen to be used as a scrubbing solvent at the Thailand 1 MWel prototype DFB gasifier at Nong Bua district in Nakhon Sawan province, Thailand.

1. Introduction

Conversion of biomass via gasification process provides the product gas that contains primarily hydrogen (H2), carbon monoxide (CO), carbon dioxide (CO2), methane (CH4), and small amount of high molecular weight hydrocarbons, known as tars. The product gas can be used for various applications such as combined heat and power (CHP), methanol production, hydrogen production, and Fischer-Tropsch (FT) liquid fuel synthesis. The dual fluidized bed (DFB) steam gasification is a promising technology of which a steam is used as a gasifying agent and to replace air in the all thermal DFB gasifier. The heat is supplied by hot circulating bed materials from the combustion zone to the gasification zone. Using steam results in a high heating value product gas with high hydrogen and methane yield, and also the reduction of tar formation [1-4].

Tars are mixtures of hydrocarbons, which are transformed into condensable tars while the product gas is cooled for downstream applications. Tars have higher molecular weight than benzene with single ring to 5-ring aromatic compounds, other oxygen-containing hydrocarbons and polycyclic aromatic hydrocarbon (PAH) compounds [5, 6]. Tars can be classified into five classes based on the molecular weight, which are (1) GC-undetectable tar determined by subtracting the GC-detectable tar fraction from the total gravimetric tar; (2) heterocyclic aromatic tar that contain hetero atom and highly water soluble; (3) light aromatics (1 ring) posing no problems for condensation; (4) light PAH compounds (2 - 3 rings), which are condensed at low temperature even at very low concentration; and (5) heavy PAH compounds (4 - 7 rings) that are condensed at high temperature and at low concentration [7, 8]. When the product gas temperature decreases, tars in the product gas will condense. The class 5 tar components condense at high temperature even at low concentration and pose the blocking problem in downstream equipment. The tar classes 2 and 4 are earlier condensed at low temperature even at very low concentration [5-8].

The tar composition and concentration depend on the type of biomass and the gasification operating conditions [7, 8]. Tar cause a main obstacle in biomass gasification because at low temperature, tar can be condensed or polymerized in piping, heat exchanger, and other equipment leading to blocking and fouling problems [5, 6]. These problems affect the performance of the system and also increase cost of operation and maintenance [7, 8]. To solve the problems, gas cleaning is necessary for tar removal in the product gas.

An oil scrubber has been developed for tar removal in downstream system [9-12]. It provides the greater tar elimination results when compared to a water scrubber [13, 14]. Phuphuakrat et al. [13] reported the removal of biomass tars by using water, diesel, biodiesel, vegetable oil, and engine oil as scrubbing solvents. Tars from wood chips were produced in the pyrolyzer at 800°C. The naphthalene removal efficiency when used the following solvents in the scrubber ranked from the highest to the lowest is diesel, vegetable oil, biodiesel, engine oil, and water, respectively. In addition, several researchers reported biodiesel has been successfully used as a based solvent for tar removal system [11, 15, 16]. Madav et al. [15] reported the performance of tar removal efficiencies in the range of 88 - 95% by biodiesel. In general, the tar removal efficiency was analyzed using one or more of three methods i.e. gravimetric, Gas Chromatography – Flame Ionization Detector (GC-FID), and Gas Chromatograph – Mass Spectrometer (GC-MS). Approximately 93% of naphthalene in producer gas was removed by packed bed scrubber when methyl oleate was used as solvent[15]. Likewise, the results from Zwart et al. [11] and Freda [16] showed the similar tar removal efficiency value when biodiesel was used as a scrubbing solvent.

In this study, we focus on finding the scrubbing solvent which can replace Rapeseed Methyl Ester (RME) in the 1 MWel prototype DFB biomass gasifier [10]. The 1 MWel prototype DFB biomass gasifier was designed and developed by Gussing Renewable Energy and it is located in Nong Bua district in Nakhon Sawan province, Thailand [10]. To reduce the operational costs and being environmentally friendly, using the local palm biodiesel as a scrubbing solvent is an attractive choice. Moreover, vegetable oil i.e. sunflower oil, refined palm oil, Thai rice palm oil, and crude palm oil, as well as diesel were investigated as alternatives to biodiesels. Five tars were used in the current work as tar representatives since they are found largely in the product gas from biomass steam gasification. The tar representatives are naphthalene, biphenyl, anthracene, fluoranthene, and pyrene [17-20]. The solubility of tar in local solvents was investigated at 30, 50, 70, and 80°C.

2. Materials and methods

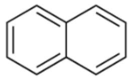
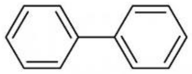
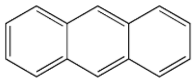
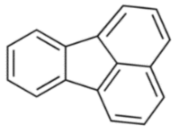
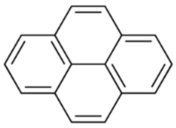
2.1 Materials

2.1.1 Simulated tars

Naphthalene, biphenyl, anthracene, fluoranthene, and pyrene were used as representatives of simulated tars from the steam biomass gasifier [17, 21-23]. Naphthalene and biphenyl represent the two ring structure compounds. Anthracene represents the three rings. Fluoranthene and pyrene are PAH classes 5 consisting of four fused benzene rings. Simulated tars were purchased from Sigma-Aldrich Pte. Ltd.

The purity of tars is greater than or equal to 98%. Details of physical properties of tar compounds are shown in Table 1.

Table 1. Physical properties of tar compounds used in this study.

Tar model	Tar class	Structure	Formula	Molecular weight	Boiling point (°C)	Melting point (°C)
Naphthalene	4		$C_{10}H_8$	128.17	218	80.26
Biphenyl	4		$C_{12}H_{10}$	154.21	256	69.2
Anthracene	4		$C_{14}H_{10}$	178.23	340	218
Fluoranthene	5		$C_{16}H_{10}$	202.25	375	110.8
Pyrene	5		$C_{16}H_{10}$	202.25	393	150

2.1.2 Solvents and its analysis

Oils used in this study consist of biodiesel, vegetable oil, and diesel. All oils employed are representatives of non-polar solvents. Biodiesel namely rapeseed methyl ester (RME) is the only oil that was imported from overseas. Other solvents can be purchased locally in Thailand. Biodiesel employed are palm methyl esters (PME), namely PME1 and PME2. Vegetable oils studied are sunflower oil, refined palm oil, Thai rice bran oil, and crude palm oil.

Measurement of solvent properties have also been experimentally conducted in this research. Density of oils was determined using Archimedes' principle. Viscosity of oils were measured by Brookfield DVIII Ultra. Gas Chromatograph-Mass Spectrometer (GC-MS) was used to analyze the components of oil. In the GC-MS analysis, oils were diluted at 100:1 in hexane except diesel that was diluted at 100:1 in acetone. The sample volume of 0.2 µL was injected into HP-5 Column. Helium was used as carrier gas at the flow rate of 0.9 ml/min. The oven temperature was stated from 40°C until the temperature reached 250℃.

2.2 Experimental setup

The 20 ml of each scrubbing solvent was filled in 50 ml beaker that was placed in 250 ml beaker of water. The beaker of water acts as a water bath, which controls the temperature of the solvent (T1) at 30, 50, 70, and 80°C by thermostat (T2). Speed of mixing using a magnetic stirrer was maintained for all conditions at 750 rpm. After the solvent temperature reached the set point, tar was gradually added into a scrubbing solvent until the just crystal appears in the solvent. This point represents the maximum tar dissolved in each solvent. Each solubility value is an average value of three repeated experimental results. A detail of the experimental setup is shown in Figure 1. Solubility value was calculated using equation 1.

IOP Conf. Series: Earth and Environmental Science **798** (2021) 012010 doi:10.1088/1755-1315/798/1/012010

$$Solubility\ value = \frac{Amount\ of\ tar\ (g)}{Volumn\ of\ solvent\ (L)} \qquad (1)$$

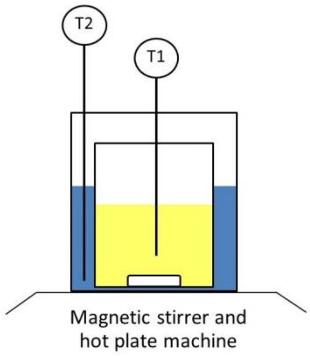


Figure 1. Experimental setup for tar solubility study

3. Results and discussions

3.1 Solvent analysis

Density and viscosity of various oils are summarized in Table 2. Chemical functional group of oil is summarized in Table 3.

Table 2. Density and viscosity of scrubbing solvents at room temperature

Solvent	Density (g/cm3) at 30°C	Viscosity (cP) at 30°C
RME	0.8817	4.93
PME1	0.8758	4.97
PME2	0.8755	4.94
Diesel	0.8380	3.46
Sunflower oil	0.9259	40.06
Refined palm oil	0.9273	52.90
Thai rice bran oil	0.9362	53.87
Crude palm oil	0.8373	1072.67

Table 3. Chemical composition of oils classified into functional group by GC-MS

Functional group/ solvent	Functional group of each oils (%wt)							
	RME	PME1	PME2	Diesel	Sunflower oil	Refined palm oil	Thai rice bran oil	CPO
Alkanes				68.673				
Aromatic				9.435				
Ester								
- Oleic acid (18:1)	73.063	40.432	29.872	12.210	23.124	41.229	39.873	39.340
- Linoleic acid (18:2)	16.391	7.766	4.497	-	45.778	10.497	27.130	7.901
- Other	8.546	50.602	64.430	9.685	28.860	40.533	24.396	49.651
Alcohol								
- Methanol	0.020	0.017	0.041					
- Glycerin	0.120	0.189	0.972		2.238	7.130	2.682	3.107
Organic acid							5.920	
Aldehyde						0.611		

3.2 Influence of solvent types on tar solubility

Based on the solubility rule, non-polar solutes are likely to dissolve in non-polar solvents. So, naphthalene, biphenyl, anthracene, fluoranthene, and pyrene are non-polar and they dissolve in non-polar solvents rather than polar-solvents. Figure 2 shows the average tar solubility in RME, PME1, PME2, diesel, crude palm oil, sunflower oil, Thai rice bran oil, and refined palm oil in gram per liter at 50°C. Each solubility value is an average value of three repeated experimental results. The trends of the solubility values are similar for all temperatures at 30, 50, 70, and 80°C. Overall, biodiesel group show the best dissolution solvent following by diesel and vegetable oil, respectively. Diesel and vegetable oil are comparable to each other. Diesel can dissolve biphenyl, naphthalene, and fluoranthene greater than vegetable oil, while pyrene and anthracene were dissolved in sunflower oil more than diesel. Among all oils, crude palm oil gives the lowest tar solubility. Almost all oils have clear color, except crude palm oil that has dark red color. Therefore, it is rather difficult for observation of tar dissolution in crude palm oil during the experiment. Discrepancy of solubility value of crude palm oil is possible.

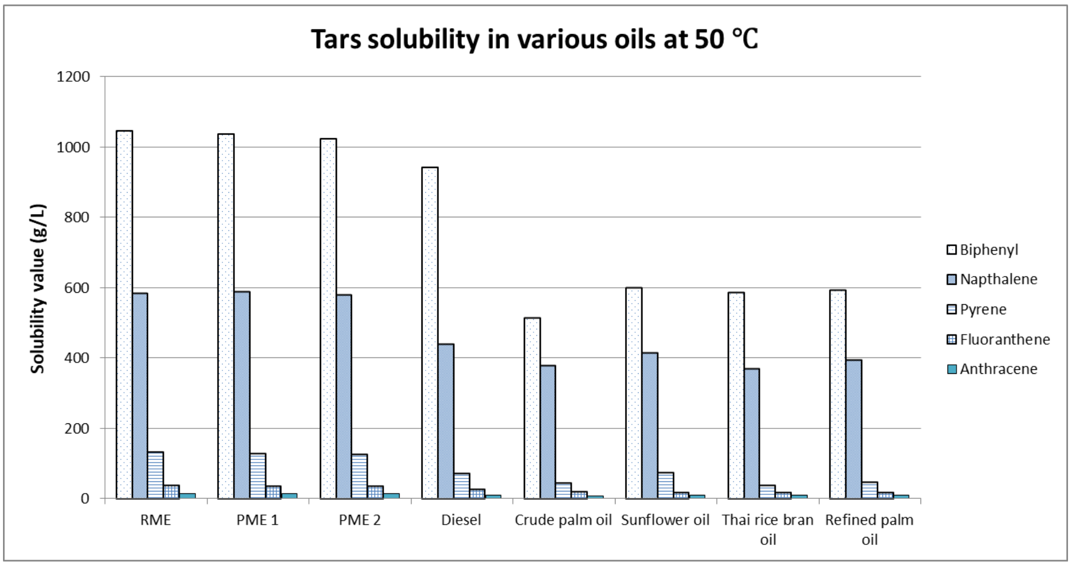


Figure 2. Average tar solubility in various oils at 50 ℃.

Density and viscosity of the solvent are also the parameters that indicate the amount of tar dissolution. Low viscosity refers to the high diffusion coefficient and dissolution rate [13, 24]. The high dissolution rate usually results in high solubility. Therefore, lower viscosity of solvent increases the solubility value. Density and viscosity of the solvents at room temperature are shown in Table 2. Diesel shows the lowest viscosity followed by biodiesel and vegetable oil, respectively. Diesel obtained the lowest viscosity at 3.46 cP, and its tar solubility is higher than that of vegetable oils and crude palm oil, except pyrene and anthracene in sunflower oil. The viscosity of biodiesel is less than vegetable oil, and crude palm oil, respectively. The viscosity of RME is the least value among three biodiesels with 4.93 cP and it shows the high tar solubility. Similar to the viscosity of sunflower oil (40.06 cP), which is the least viscosity value of all vegetable oils, it can dissolve tar more than refined palm oil and Thai rice bran oil with viscosity of 52.90, and 53.87 cP, respectively.

Chemical functional group of oils is another parameter relating to the tar solubility, and it is summarized in Table 3. Most oils consist of ester group, except for diesel, which mainly contains alkanes. When ranking the polarity of functional group from the highest to the lowest, it can be arranged as follows: amide > organic acid > alcohol > aldehyde > ketone > amine > ester > ether > alkane. Considering the biodiesels, ester group is the main functional group in all three biodiesels. Although RME has the weight percentage of ester group less than PME1 and PME2, oleic acid in RME is the highest value when compared with the other oils including PME1 and PME2. Oleic acid

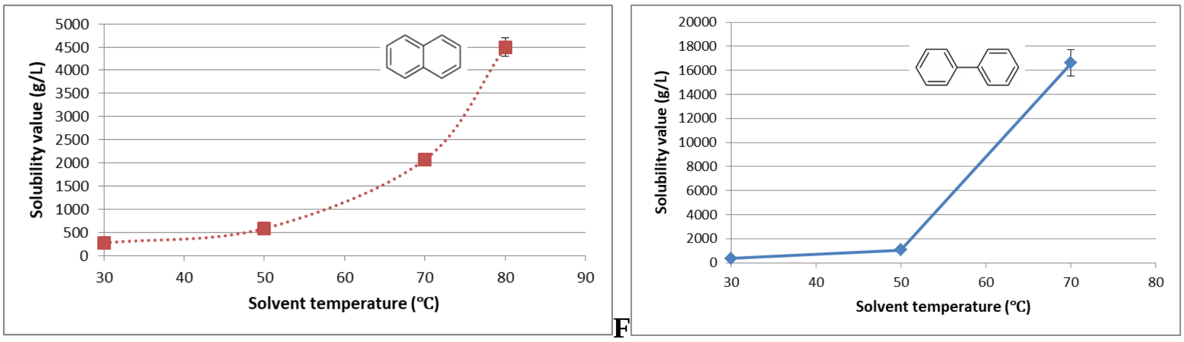
IOP Conf. Series: Earth and Environmental Science **798** (2021) 012010 doi:10.1088/1755-1315/798/1/012010

is a non-polar substance while linoleic acid is a polar substance [12, 25]. Therefore, RME can dissolve tar, which are non-polar, more than PME1 and PME2. A main compound of diesel is the straight-chain alkanes which have less number of carbon atoms than carbon atoms in ester group of biodiesel. Incrementing the length of hydrocarbon chain increases the solubility value in non-polar solvents [26]. Thereby, diesel can dissolve tar less than biodiesel. Although vegetable oil has high percentage of ester group, it also has high alcohol and organic acid group more than the other oils. Increment of alcohol and organic acid increases the polar substance in vegetable oil. Thus, tar dissolves in vegetable oil less than biodiesel due to increment of polar substance and high viscosity of vegetable oil as described earlier.

3.3 Influence of tar molecular structure on tar solubility

Solubility is the maximum solute that can dissolve in a solvent which is measured as the saturated concentration at constant pressure and temperature. The quantity of solute dissolving in solvent depends on intermolecular forces between solute-solute, solute-solvent, and solvent-solvent. Interaction of solute-solute is mentioned in this section.

The melting point of solute is a basic property to estimate the solubility process. Low melting point refers to the low intermolecular force of solute and thus high solubility in the solvent [27]. The melting points of five tars can be ranked from lowest to highest follow: biphenyl (69.2°C) < naphthalene (80.6°C) < fluoranthene (110.8°C) < pyrene (150°C) < anthracene (218°C). Biphenyl shows the lowest melting point and the highest solubility in all solvents and at all temperatures (see Figure 2 and Figure 3). Naphthalene has lower melting point than fluoranthene, pyrene, and anthracene while naphthalene solubility is higher than fluoranthene, pyrene, and anthracene. Solute-solute interaction or defined as Van der Waals interaction of naphthalene (172 meV) is less than Van der Waals of anthracene and pyrene with 245, and 282 meV, respectively [28]. The low Van der Waals causes breaking solute-solute interaction easier. Thus, naphthalene solubility is higher than anthracene, pyrene, and fluoranthene solubility as shown in Figure 2.



(a) **(b)**

Figure 3. Naphthalene and biphenyl solubility in RME, (a) Naphthalene, (b) Biphenyl.

Figure 4 presents the solubility of pyrene, fluoranthene, and anthracene in RME at 30, 50, 70, and 80°C. Pyrene shows the highest solubility among the three tars. Fluoranthene solubility is higher than anthracene solubility. As compared the melting point, fluoranthene and pyrene have lower melting point than anthracene. In addition, heat of fusion of anthracene is higher than fluoranthene and pyrene with 29.4, 18.73, and 17.36 J mol-1, respectively [29]. Therefore, the highest melting point and heat of fusion of anthracene causes the lowest solubility of anthracene in various oils. Fluoranthene and pyrene are isomerism which both tars have similar properties, i.e. melting point and heat of fusion. Due to limitation of solubility data of fluoranthene and pyrene in the literature, it is rather difficult to explain the results of these experiments.

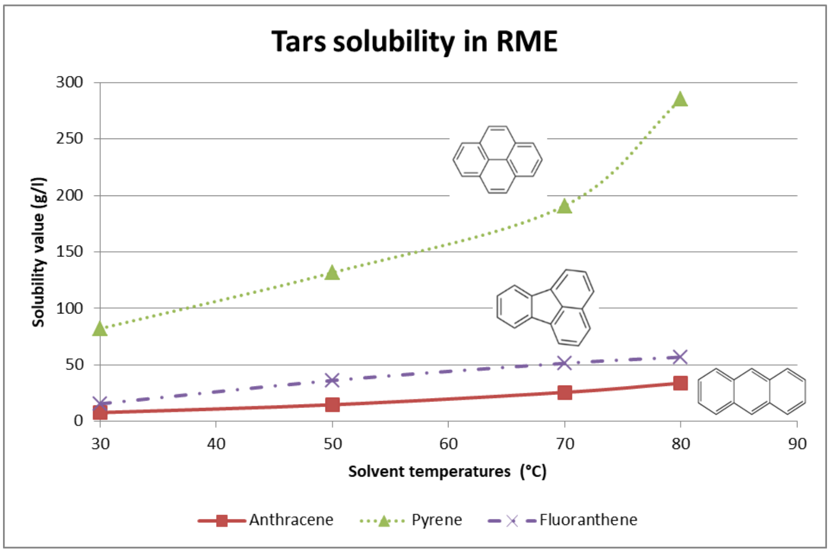


Figure 4. Anthracene, pyrene, and fluoranthene solubility in RME.

3.4 Influences of solvent temperature on tar solubility

Naphthalene and biphenyl comprise two benzene rings. Both tars are classified into class 4 and have the melting point near the operating temperature of the oil scrubber at 45-55°C in the Nong Bua DFB gasification process. Figure 3 displays the naphthalene and biphenyl solubility in RME at different temperatures. Naphthalene solubility was slightly increased from 30 to 70°C while biphenyl solubility was rapidly increased when solvent temperature increased from 50 to 70°C. The biphenyl solubility was rapidly increased at 70°C because it reaches the melting point of biphenyl at 69.2°C. The melting point is defined as the temperature that breaks the solid particle and changes from solid into liquid state. Therefore, biphenyl solubility was rapidly increased when solvent temperature was raised to 70°C. Figure 4 presents anthracene, pyrene, and fluoranthene solubility in RME at different temperatures in a range of 30 to 80°C. Tar solubility increases with solvent temperature increases. This phenomenon can be explained by the endothermic reaction occurred during dissolving and thus solubility values increased with temperature.

4. Conclusion

The solubility of five tar compounds was investigated in various oil solvents at different temperatures from 30 to 80°C. Naphthalene, biphenyl, anthracene, pyrene, and fluoranthene were employed in this study as the representatives of tar compounds in the DFB biomass steam gasification of wood biomass. Among all of the oil solvents, biodiesel can effectively dissolve all tar compounds due to its low viscosity and high non-polar substances. Therefore, biodiesel is chosen as the suitable solvent for tar removal in terms of removal efficiency, costs, and environmental impacts. In addition, higher temperature results to higher tar solubility in the biodiesel, and thus the optimum operating temperature of the scrubber needs to be further investigated in terms of the tar removal efficiency and safety issues.

5. References

[1] Pfeifer C 2013 *Fluidized Bed Technologies for Near-Zero Emission Combustion and Gasification* (Fabrizio Scala) Woodhead Publishing 971-1001
[2] Sutton D, Kelleher B, and Ross J R H 2001 *Fuel Process. Technol* **73(3)** 155-173
[3] Shahbaz M, Yusup S, Inayat A, Patrick D O, and Ammar M 2017 *Renew. Sust. Energ. Rev.* **73** 468-476
[4] Loha C, Chatterjee P K, and Chattopadhyay H, 2011 *Energy Convers. Manag.* **52(3)** 1583-1588

[5] Neeft J P A, Knoef H, Stichting E C N, and B T G 1999 *Behaviour of tar in biomass gasification systems: tar related problems and their solutions* Utrecht Maarn Novem MHP Management & Secretary Services [distr.]
[6] Devi L, Ptasinski K J, and Janssen F J J G 2003 *Biomass Bioenerg*. **24(2)** 125-140
[7] Milne T A, Evans R J and Abatzaglou N 1998 Biomass Gasifier "Tars":Their Nature, Formation, and Conversion (United States)
[8] Li C and Suzuki K 2009 Renew. Sustain. Energy Rev. 13(3) 594-604
[9] Hofbauer H, Rauch R, Bosch K, Koch R and Aicherning C 2002 Pyrolysis and Gasification of Biomass and Waste
[10] Hongrapipat J, Messner M, Henrich C, Koch M, Nenning L, Rauch R, and Hofbauer H 2015 *Conference: Renewable Energy World Asia Conference 2015*
[11] Zwart R, Drift B, Bos A, Visser H, Cieplik M, and Könemann H W J 2009 *Environ. Prog. Sustain. Energ.* **28** 324-335
[12] Ahmad N A and Zainal Z A 2016 *J Nat Gas Sci Eng* **32** 256-261
[13] Phuphuakrat T, Namioka T, and Yoshikawa K 2011 *Bioresour. Technol* **102(2)** 543-549.
[14] Balas M, Lisy M, Zdenek A, and Pospisil J 2014 *Adv Environ Sci Dev Chem* 195-201.
[15] Madav V, Das D, Kumar M, Surwade M, Parikh P P, and Sethi V 2019 *Biomass Bioenerg* **123** 123-133
[16] Freda C, Fanelli E, Nanna F, Canneto G, Braccio G, and Barisano D 2010 *Proceedings of the 18th European Biomass Conference and Exhib* 3-7
[17] Kirnbauer F, Wilk V, Kitzler H, Kern S, and Hofbauer H 2012 *Fuel* **95** 553-562
[18] Devi L, Ptasinski K J, and Janssen F J J G 2005 *Ind. Eng. Chem. Res.* **44(24)** 9096-9104
[19] Wang Q, Li Q, Tsuboi Y, Zhang Y, Zhang H, and Zhang J 2018 *Fuel Process. Technol.* **182** 88-94
[20] Li Q, Wang Q, Kayamori A, and Zhang J 2018 *Fuel Process. Technol.* **178** 180-188
[21] Aigner I, Wolfesberger U, and Hofbauer H 2009 *ICPS 09*
[22] Mauerhofer A M, Schmid J C, Benedikt F, Fuchs J, Müller S, and Hofbauer H 2019 *Energ.* 173 1256-1272
[23] Zhang Z and Pang S 2019 *Renew. Energy* **132** 416-424
[24] Ozturk B and Yilmaz D 2006 *Process Saf Environ Prot* **84(5)** 391-398
[25] Thapa S, Indrawan N, Bhoi P R, Kumar A, and Huhnke R L 2019 *Energ.* **175** 402-409
[26] Muzenda E 2014 *IJCEBS* **2(2)** 113-117
[27] Batisai E, Ayamine A, Kilinkissa O, and Báthori N 2014 *CrystEngComm* **16**
[28] Chakarova S and Schröder E 2005 *J. Chem. Phys.* **122(5)** 54102
[29] Roux M V, Temprado M, Chickos J S, and Nagano Y 2008 *J Phys Chem Ref Data* **37(4)** 1855-1996

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