Effect of Temperature on Catalytic Decomposition of Tar using Indonesian Iron Ore as Catalyst

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Abstract- In pyrolysis, tar is undesired byproduct because it causes operational problems such as the contamination in the inner wall of a reactor, blockages in pipes, corrosion and formation of tar aerosols and carcinogenic. Therefore, it is necessary to take steps for removing or decomposing tar into fuel gas (bio-syngas) and other compounds that are more useful. In this experiment, catalytic process was selected to decompose tar derived from wood waste pyrolysis. The study was focused on the effect of temperature on catalytic tar decomposition using a fixed bed reactor with using Indonesian iron ore as catalyst. Initially, tar was vaporized inside preheater at temperature of 450°C, and then was passed through the catalyst bed. The variables studied were temperatures between 500 – 700°C and height of catalyst bed between 0.67 – 1.34 cm. Yields of gas, bio-oil, char and aqueous and also compositions of gas and liquid product were evaluated. The liquid product are represented in terms of acid compounds, hydrocarbon compounds, ketone compounds, oxygenate compounds, aromatic hydrocarbon - one cyclic (AH-1), poly aromatic hydrocarbon - two cyclic (PAH-2) and poly aromatic hydrocarbon - three cyclic (PAH-3). The results showed that the yields of gas and char increased by increasing temperature from 500 to 700°C, while bio-oil decreased. In addition, increasing temperature resulted new compounds of AH-1, PAH-2 and PAH-3. The yields of PAH-2 and PAH-3 on liquid product and hydrogen and methane on gas product also increased, while yields of acid, ketone, AH-1 decreased.

Keywords Tar, biomass, catalytic decomposition, low grade iron ore.

1. Introduction

To date, the world's energy resources are still dominated by fossil fuel consisting of oil, gas and coal. The use of fossil fuels will continually face challenges including depletion of fossil fuel reserves, raise of fuel price, global warming and other environmental concerns [1;2]. These facts indicate an unsustainable situation for energy saving and cost reduction [3;4]. Biomass energy can be considered as one of the solutions to the growing energy challenges as it is abundant, inexhaustible and environmentally friendly [5-7]. Biomass can be converted into energy (power generation and transportation fuels) and chemical feedstock [8]. Conversion of biomass into energy can be achieved by using two main process technologies: biochemical and thermo-chemical [9]. Biochemical conversion consists of two major processes: digestion and fermentation. While under thermo-chemical conversion, four process options are available: combustion, pyrolysis, gasification, and liquefaction [10;11]. Pyrolysis has several advantages namely, simple reactor configuration,

faster reaction time, more liquid products (less energy for product separation) and high adaptation to various biomass [12;13].

Pyrolysis involves degradation of biomass by using the heat in absence of air at temperature 500 – 900°C which is relatively lower compared to gasification (800 – 1500°C) [14]. Pyrolysis process produces gas, char and tar [15]. Char is the main product that is used as reducing agent, while tar and gas are byproduct containing carbon and substantial energy [16]. Tar is liquid phase which different from gas and char, because it contains more than 100 compounds especially that produced from pyrolysis at around 800 K [17]. In pyrolysis, tar is a product which is not desirable, because it causes operational problems such as contamination in inner wall of a reactor, blockages in pipes, corrosion and formation of tar aerosols [18] and also carcinogenic [19]. Therefore, it is necessary to take steps for removing or decomposing tar into fuel gas (syngas) and other compounds that are more useful. The ways to remove tar are physical, non-catalytic and catalytic [20]. Chemical conversion by catalytic process is more likely to be opted, because it can convert tar component into valuable products at lower temperature [21;22].

The decomposition of tar is usually carried out at a temperature between 500 – 900°C and by using a catalyst such as olivine, dolomite, limestone, metal oxides, Ni and Rh / Pt / Pd [23-26]. In its application, the catalyst for tar decomposition depends on its composition and type. Han and Kim mentioned that the catalyst is divided into 4 groups: (1) Ni-based catalysts; (2) alkali metal catalysts (Rh, Ru, Pd, Pt, Fe, etc.); (3) dolomite catalyst; (4) novel metal catalyst [27]. The performance of the highest catalyst can be defined as Rh> Pt> Pd> Ni = Ru [25]. However, Rh catalyst is much more expensive [28]. The dolomite catalyst is less suitable for tar decomposition because of its high chlorine content, while the dolomite containing Ca of which could react to CaCl₂ and causing the catalytic activity to decrease [29]. While the Ni-based catalyst is expressed as the most effective catalyst, especially in the process of steaming reforming methane but it has high rate of deactivation and high price [30].

Recently, Fe-based catalyst has been a concern to some researchers. It has been demonstrated that Fe-based catalyst has the ability to process catalytic cracking of tar. This catalyst is slightly sensitive only to chlorine and produces a cleaner gas [29]. In addition to its ability to reduce tar, it could be synergized in iron-making process [31;32]. Liu et al. [33] in his study stated that Fe impregnated into Ni / Polygorskite clay was better than the Mg, Mn and Ce. Virginie et al. [34] studied the Fe / olivine for tar decomposition process for biomass gasification in fluidized bed and it was concluded that Fe / olivine can lower the levels of tar and increase the production of syngas. The existence Fe olivine is believed to make the catalyst more active, so its use is very promising because it is cheap and non-toxic. Kudo et al. [35] stated that the process using natural iron ore is proven effective to produce clean syngas (free of tar) and the results of the analysis of tar from the pyrolysis process is less than 0.01%.

Low grade-iron ore, that has been dehydrated, is proven to be usable firstly as a catalyst in the decomposition of tar

result of pyrolysis or gasification [32;36]. Simultaneously, through the process of tar decomposition, carbon would then enter and be deposited in the pores of the iron ore to produce composite carbon-iron ore. Carbon deposits in the pores of iron ore obtained from tar decomposition process shows a good influence on the iron ore reduction process [16]. According to Hosokai et al. [37], the reduction reaction with composite iron ore - carbon requires low reduction temperature (750°C) compared to the conventional one which requires a temperature up to 1200°C. This is caused by the carbon deposited into the pores of iron ore has a smaller size, thereby increasing the surface area to have reaction. Consequently, this process can produce high-speed reduction, lower temperature, and reduced energy consumption.

The objective of this research is to investigate the effect of operation temperature of catalytic decomposition of tar carried out in a fixed bed reactor. We used iron ore from Indonesia which is available abundantly and includes low grade iron ore. It is expected the iron ore can be utilized in iron making industry after tar decomposition process. In addition to containing Fe, the iron ore also contains silica and alumina which can act well as a catalyst in the catalytic cracking of bio-oil [22]. Yields of product, compositions of syngas and quality bio-oil were studied and tar product was classified based on the work by Milne et al. [38].

2. Materials and Methods

2.1. Materials

Tar used in this study was derived from pyrolysis of wood waste with heating value of 28.77 MJ/kg and density of 1.009 gr/cm³. While low grade iron ore was obtained from Limited Liability Company SILO (*PT*. SILO /Sebuku Iril Laterit) in Sebuku Island, Kotabaru, South Kalimantan, Indonesia. The compositions of low grade iron ore were 51.41 % of total Fe, 7.214 % of Al₂O₃, 3.042 % of SiO₂ and 0.4803 % of NiO.

Classification of raw material tar of this work is shown in Table 1. Raw materials were grouped based on the acid groups, hydrocarbons, ketones, compounds oxygenate and tar. Tar contained in the feedstock consisting of phenol compounds and pyridine both of which were formed a ring of a heterocyclic compound.

2.2. Apparatus

Figure 1 shows the experimental equipment for tar decomposition. The apparatus was equipped with a vaporizer to ensure the oil enters the reactor in the vapor phase and a condenser set to change condensable vapor to liquid. The experiment was conducted in a fixed bed rector with catalyst bed height range of 0.67 to 1.34 cm at temperature of 500 to 600°C.

2.3. Experiment Procedure

Initially, nitrogen was passed through the reactor and preheater to remove oxygen. The reactor and vaporizer were heated by electrical heating system and the temperature was

controlled by digital temperature controller. Once the temperature inside the reactor and vaporizer has reached steady condition at specified temperature, the tar was flowed into the vaporizer to produce vapor. Then, the vapor passed through the catalyst bed and resulted in catalytic reaction. Subsequently, the vapor left the reactor and entered the cooling system.

Table 1. Classification of raw material tar

Compound	Formula	Percentage
Acid		40.07
Acetic Acid	$C_2H_4O_2$	4.68
Decanoic Acid	$C_{10}H_{20}O_2$	0.33
Dodecanoic Acid. Methyl Ester	$C_{13}H_{26}O_2$	4.41
Dodecanoic Acid	$C_{12}H_{24}O_2$	23
2-Propenyl Nonanoate	$C_{12}H_{24}O_2$	0.46
Tetradecanoic Acid. methyl	$C_{15}H_{30}O_2$	1.74
Tetradecanoic Acid	$C_{14}H_{28}O_2$	3.06
Hexadecanoic Acid. methyl	$C_{17}H_{34}O_2$	1.52
Hexadecanoic Acid	$C_{16}H_{32}O_2$	0.37
10-Octadecanoic Acid. methyl	$C_{19}H_{36}O_2$	0.5
Hydrocarbon		1.22
Hexadecane	$C_{16}H_{34}$	0.31
5-Eicosene	$C_{20}H_{40}$	0.22
Eicosane	$C_{20}H_{42}$	0.18
Undecanenitrile	$C_{11}H_{21}N$	0.51
Ketone		2.83
Propanon/ Aceton	C_3H_6O	2.83
Mixed-Oxigenated		7.00
Benzene, 1,4-dimethoxy	$C_8H_{10}O_2$	4.42
Phenol 2,6-dimethoxy	$C_8H_{10}O_2$	0.83
2,4-Hexadienedionic Acid	$C_{12}H_{18}O_4$	0.93
1,2-Benzenedicarboxylic acid,	$C_{24}H_{38}O_4$	0.82
Phenol and Alkyl		48.84
Phenol	C_6H_6O	33.64
Phenol, 2-methoxy-	$C_6H_7O_2$	4.12
Phenol, 2,3-dimethyl-	$C_8H_{10}O_2$	0.84
Phenol, 4-ethyl-2-methoxy-	$C_9H_{12}O_2$	2.95
Phenol, 2,6-dimethoxy-	$C_8H_{10}O_3$	4.37
Other		2.92
Pyridine, 3-methyl-, 1-oxide	C_6H_7NO	2.92

There were the two phases which obtained from the condenser, aqueous and organic liquid phase. Besides the product in the liquid phase, the cracking reactions also produced gas which its volume was measured by the displacement volume of water. The reaction was continued until no more liquid product was condensed. The composition of the liquid and gas product was analyzed using Gas Chromatography and GC-MS. The effectiveness of catalyst was evaluated by performing experiments opting various ratios of catalyst bed height and reaction temperature.
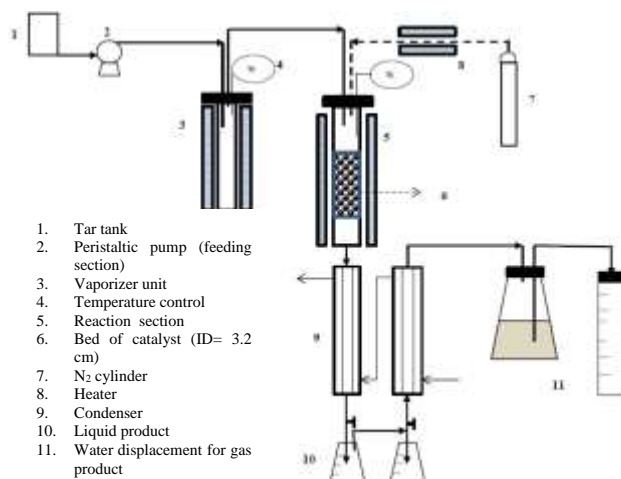

1. Tar tank
2. Peristaltic pump (feeding section)
3. Vaporizer unit
4. Temperature control
5. Reaction section
6. Bed of catalyst (ID= 3.2 cm)
7. N_2 cylinder
8. Heater
9. Condenser
10. Liquid product
11. Water displacement for gas product

Fig. 1. Experiment apparatus for tar decomposition

3. Result and Discussion

3.1. Effect of temperature on yield of product

In this study, the effect of temperature on product yield that was studied in the range of 500 to 700°C and the catalyst bed heights of 0.67 to 1.34 cm is shown in Fig.2. From this figure we may see that while temperature increased, the yield of bio-oil decreased and gas and char increased. By increasing the temperature from 500 to 700°C, gas yield increased from 32.2 to 76.02 % for (a) and 34.3 to 86.76 % for (b), respectively. The bio-char increased from 0.56 to 2.98% for (a) and 1.38 to 3.32 % for (b). While the bio-oil declined from 59.76 to 15.20 % for (a) and from 58.28 to 7.24 % for (b).

The increase in gas yield and the decrease in bio-oil yield indicate that the rate of tar decomposition reaction increases along with the increasing temperature [42]. In addition, at elevated temperature, tar conversion increased and made decomposition to the gas product easier [19]. By increasing the temperature, bio-oil which is dominated by phenol tar, acid and oxygenated compounds will be converted into compounds of light hydrocarbons like methane (CH_4), hydrogen (H_2), carbon dioxide (CO_2) and carbon monoxide (CO).
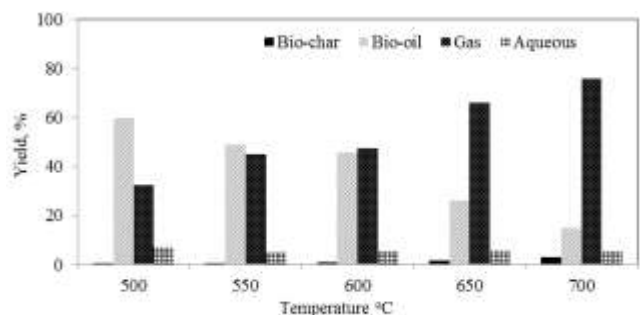
(a) Catalyst bed height 0.67 cm
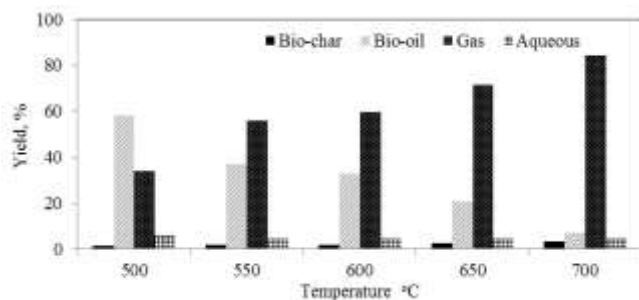
(b) Catalyst bed height 1.34 cm

Fig. 2. Effect of temperature on yield of product.

3.2. *Effect of temperature on composition of gas product*

The main gas components resulted in tar catalytic decomposition were CO, CO_2, H_2 and CH_4. Figure 3 shows composition of gas products from this process. From this figure we may see that contents of CO, CO_2, H_2 and CH_4 increased along with the increasing temperature. H_2 and CH_4 increased from 1.88 to 17.06 % and 3.92 to 12.67 %, respectively. CO_2 fluctuated with range of 2.36 to 3.06 %. CO increased from 9.19 to 14.64% at temperature of 500 - 550°C and dropped to 12.59% at temperature of 550°C and then climbed up to 20.82% at temperature 700°C. The phenomenon of decrease CO at temperature of 600°C was probably caused by increasing activity of reduction reaction of CO to CO_2. In addition, it was also probably due to increasing in the water-gas shift reaction, where steam was produced to break deoxygenated reaction into hydrocarbon [40]. Increasing H_2 yield at elevated temperature improved the syngas quality. High content of H_2 increased the heating value of the gas product [14]. This result agreed with the data reported Virgine et al. that Fe catalyst can gave the better quality of syngas [41].
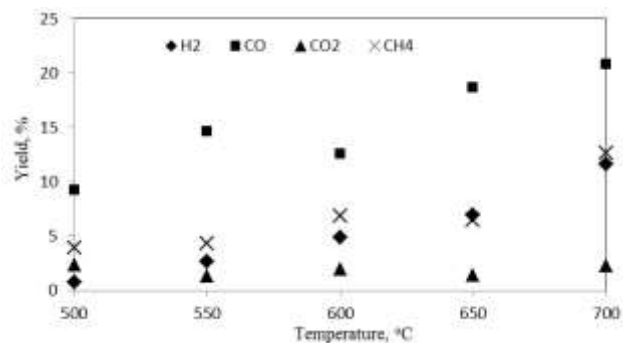

Fig. 3. Effect of temperature on composition of gas product.

3.3. *Effect of temperature on composition of tar compounds*

3.3.1. *Primary tar compound*

The class of the primary tar is characterized by acid, aliphatic hydrocarbon, ketone and mixed-oxygenated compounds. The thermal behavior of selected compounds in this class during the experiment of tar decomposition at different temperatures is shown in Fig.4. As it is commonly well known that the yields of acid compounds decrease almost linearly along with the increasing temperature, where this also happened in Fig.4. There it can be seen that the hydrocarbon compounds decreased slightly in the temperature range of 500 – 600°C and then decreased sharply at the temperature of 650°C. The yields of ketone compounds also decreased slightly in the temperature range of 500 – 600°C and then remained relatively stable at the temperature of 650°C. The yields of mixed-oxygenated compounds remained stable along with the increasing temperature. When the conversion of primary tar compounds was calculated, the maximum conversion of aliphatic-hydrocarbon, mixed-oxygenated, acid and ketone compounds were approximately of 96, 94, 92 and 89%, respectively, at the temperature of 650°C. Overall, the high conversion of primary tar compounds, especially aliphatic-hydrocarbon ones, can be considered as a logical consequence of the ability of chemical bonds of primary tars to be easily broken down when being compared to complex compounds.
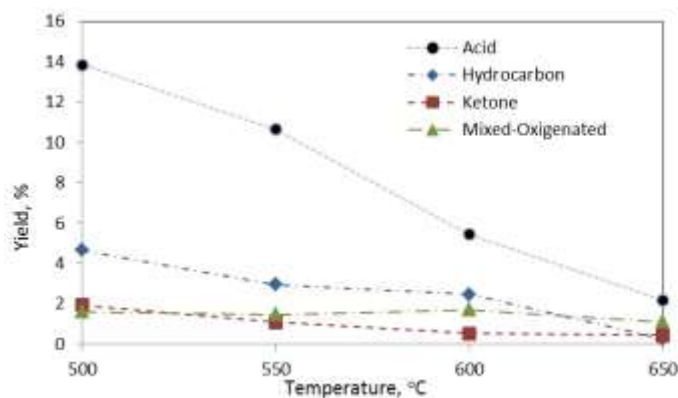

Fig. 4. Effect of temperature on composition of primary tar compounds.

3.3.2. Secondary tar compounds

The secondary tar compounds consist of phenol, benzene, alkyl benzene and toluene. In this experiment, the phenol compound was most found in raw tar, approximately 34% (see Table 1). The yield of phenol with different temperatures during the experiment of tar decomposition was shown in Fig. 5. It was seen that the yield of phenol decreased linearly along with the increasing temperature, whereas the alkyl phenol slightly increased until temperature 550°C and then decreased linearly. It was stated in previous studies that the phenolic compounds were identified as precursors for the formation of PAH, especially naphthalene [42]. The result of conversion calculation showed that the maximum conversion of phenol was 54% at temperature of 650°C.

The tar decomposition processes would produce the new compounds of aromatic hydrocarbon. Figure 6 shows the yields of new secondary tar compounds during the experiment of tar decomposition at different temperatures. It is seen that the compounds of benzene, alkyl benzene, toluene and indene were formed early at temperature of 500°C. The yields of them increased until to temperature of 600°C and then sharply decreased at temperature of 650°C, whereas compounds of benzo-furan and di benzo-furan began to form at temperature of 550°C. The yield of benzo furan decreased at temperature of 600°C and then increased at temperature of 600°C. The yield of di benzo furan remained stable until to temperature 650°C. The new secondary tar compounds may be produced from decomposition of the primary tar.
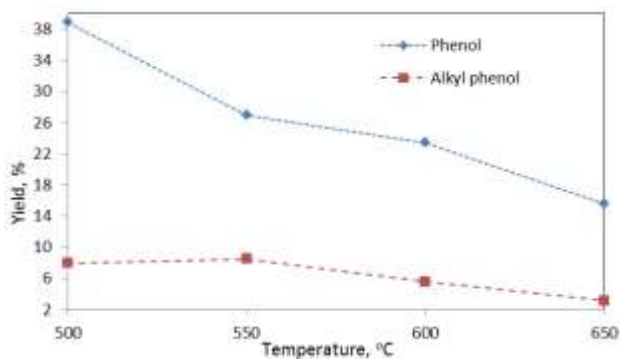

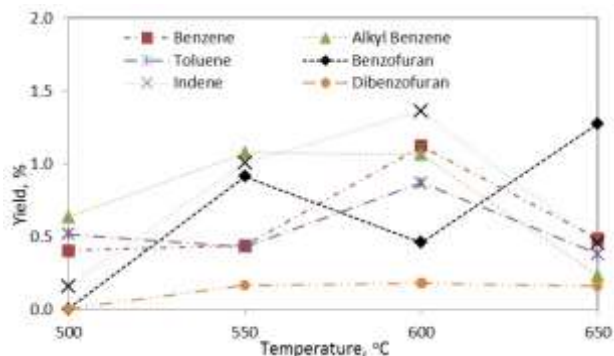**Fig. 5.** Effect of temperature on concentrations of phenol.

Fig. 6. Effect of temperature on concentrations of secondary tar compounds.

3.3.3. Tertiary tar compounds

The tertiary tar compounds consist of Poly Aromatic Hydrocabon (PAH) ring 2 or more. The thermal behavior of selected compounds in this class during the experiment of tar decomposition at different temperatures is shown in Fig.7 (for 2-ring PAH) and Fig.8 (for 3-ring PAH). Figure 7 shows that naphthalene and alkyl naphthalene increased linearly while temperature increased. Figure 8 shows that naphthalene was produced at temperature 550°C and then the yield increased, whereas pyrene started to form at temperature at 650°C. It is also shown that more PAH were formed along with the increasing temperature. Various theories on the formation of PAH are studied in literatures. As Frenklach and Wang stated the growth of aromatic to higher moleculer compounds is explained by a mechanism consisting of two reaction pathways: (a) direct combination of intact aromatic rings, as example the combination of two benzene rings leads to biphenyl,which reacts further towards PAH compounds, (b) H_2-abstraction-C_2H_2-addition (HACA) sequence [43]. Aromatic rings grow through H-abstraction, which activates the aromatic molecules, an acetylene addition, which propagates molucular growth by cyclication.
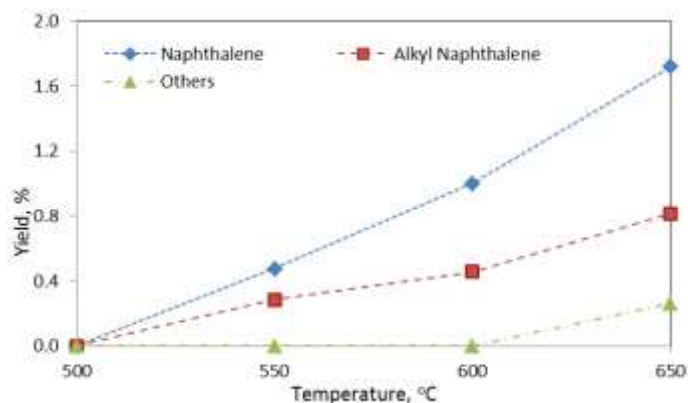

Fig. 7. Effect of temperature on concentrations of 2-ring tertiary tar compounds.
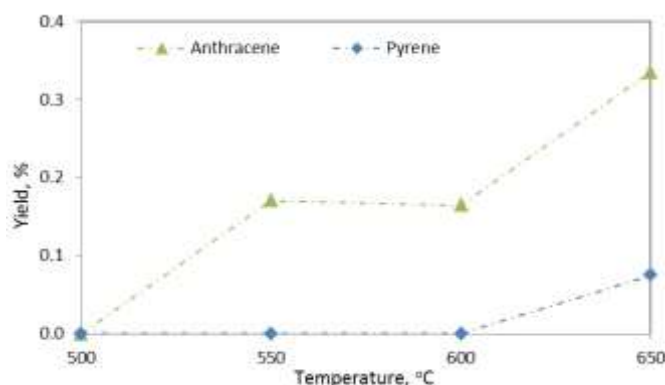

Fig. 8. Effect of temperature concentrations of 3-ring tertiary tar compounds.

4. Conclusion

The Indonesian low grade iron ore had good performance as catalyst on tar decomposition. The iron ore also contents silica of 3.042% and alumina of 7.214%. The result show that at temperature of over 550°C, the gas product was found to be the highest compared to the others. The temperature of catalytic decomposition also had influence on composition of gas product on tar catalytic decomposition. With the increasing of temperature from 500 to 700°C, content of H_2, CH_4, CO_2 and CO tended to increase and ratio H_2/CO also increased from 0.21 to 0.83. Besides that, increasing temperature resulted to the creation of new compounds of AH-1, PAH-2 and PAH-3. The yields of PAH-2 and PAH-3 on liquid product increased, while yields of acid, ketone and AH-1 decreased. With decreasing oxygenated compounds (acid, phenol and ketone) and increasing hydrocarbon compounds upgraded quality of bio-oil.

Acknowledgements

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