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Atmospheric Hydro-cracking of Jatropha Oil Using Wood Char Catalyst

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Abstract

Jatropha oil which is non-edible oil were hydro-crack at atmospheric pressure using an activated wood char catalyst in a fixed bed reactor. The hydro-cracking process was carried out at three temperature variations of 400, 450 and 500ºC, and three variations of the oil feed injection rate of 2/2, 2/5 and 2 mL/10 minutes. The catalysts were characterized using SEM and BET. The composition of the liquid product obtained from the hydro-cracking process was analyzed using GC-MS. The effects of operating temperature and oil feed injection rate on oil recovery and conversion have been discussed. The results showed that the feed injection temperature and rate had an effect on the yield and conversion. The highest yield of 59.8% oil liquid products was achieved at a temperature of 450ºC with injection rate of 2 mL/10 min. The composition of the oil-liquid product was dominated by heptanal at 32.9% -mass. Alkanes group contain C_5 to C_{20} and alkene compounds consist of C_8 until C_{18}.

INTRODUCTION

Jatropha oil is a non-edible that can be obtained from the compression of Jatropha beans or extraction using solvents. The oil content in Jatropha beans ranges from 25%-45% depending on the variety and environmental conditions. Jatropha plants can grow well in tropical and subtropical climatic conditions with plant heights of around 3-6 meters (Gudeta, 2016). Jatropha oil has the potential to become a resource of renewable raw material for fuel oil production. The fuel that can be made from Jatropha oil is methyl ester (bio-diesel) (Wardhani & Hidayat, 2014; Shaaban et al., 2016; Folaranmi, 2013). The disadvantage of bio-diesel is cannot be used in the engine with 100% composition, due to can be damaged engine in the long term use (Parawira, 2010). Therefore, at this time researchers began to develop green gasoline, green avtur and green diesel using jatropha oil as raw material with catalytic cracking process (Saxena & Viswanadham, 2016; Liu et al., 2015; Mijan et al., 2017). These green fuel has the same properties as fossil fuels, so there is no need to change the existing vehicle engine.

There are several methods to convert Jatropha oil into green fuel. Hydro-cracking is one method to produce green fuel from Jatropha oil with introduction of hydrogen for remove oxygen atoms from oil structure with the release water, carbon monoxide and carbon dioxide. Commonly, hydro-cracking of Jatropha oil carried out at high pressure with high activity catalyst. Some researchers have reported hydro-cracking of Jatropha oil using metal catalyst. Yang et al. (2017) use PTA-NiMo/ZSM-5 catalyst with 30 bar of pressure. Liu et al. (2013) was studied Ni-HPW/Al_2O_3 catalyst to transform Jatropha oil to primarily C_{15}-C_{18} alkanes with operating pressure condition is 33 bar.

Activity of some metal catalyst is high, but these catalysts difficult to make it and very limited due to the availability and high price. Therefore, it is necessary to develop catalysts that are

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Table 1. Physical properties of Jatropha oil.

Properties	Pramanik (2003)	Aminul Islam (2012)	Singh (2009)	Anthony Raja (2011)	This research
Density (g/cm^3)	0.933^{30C}	0.917^{20C}	0.918^{15C}	0.920	0.98^{25C}
Kinematic viscosity (cSt)	52.76^{30C}	-	32^{40C}	40.4^{31C}	-
Flash point, ^{o}C	210	-	186	214	273
Calorific value, MJ/kg	38.20	39.5	33	39.76	-

inexpensive, easily available and where possible are renewable. Wood activated carbon has the potential to be a hydrocracking catalyst that is renewable, easily made or obtained and inexpensive. Micro-structure of wood activated carbon has vertically aligned micro-channels like a sieve, maybe this is can be as a function to screen molecule and cut the oil to short molecule (Cheng & Li, 2018).

In this study, Jatropha oil will be hydro-cracked using wood activated carbon in a fixed bed reactor. The effect of operating condition likes the reaction temperature, Jatropha oil flow rate injection, hydrogen flow rate on the liquid product (OLP) yield, the gas product yield, properties of the liquid product such as pH, density, kinematic viscosity and compositions is discussed.

MATERIALS AND METHODS

Materials

Jatropha oil that has been used in this study was obtained from an online store in the Cimahi. The physical properties of Jatropha oil are presented in Table 1. The density of Jatropha oil varied from 0.92 - 0.98 g/cm^3. Kinematic viscosity varied from 32 - 52.76 cSt. Flash point of Jatropha oil was used relatively higher than literature.

The composition of Jatropha oil is presented in Table 2. The major of fatty acids in the Jatropha oil which are palmatic acid, stearic acid, oleic acid and linoeic acid. Other material in this research is hydrogen. Hydrogen that has been used obtained from shop in the Bandung with 30%-vol (N_2 balanced).

Table 2. Composition of Jatropha oil.

Fatty acid	Akbar (2009)	Anthony Raja (2011)
Palmatic acid ($C_{16:0}$)	14.2%	4.2%
Stearic acid ($C_{18:0}$)	7.0%	6.9%
Oleic acid ($C_{18:1}$)	44.7%	43.1%
Linoleic acid ($C_{18:2}$)	32.8%	34.3%
Other acids	1.3%	1.4%

Catalyst preparation and activation

Wood char was obtained from a small shop in Cimahi then reduced of size to average diameter 1.5 mm. Thermal method was used to activated of wood char. Where the wood char was heated slowly at a heating rate of 5^{o}C/min until it reached temperature of 400^{o}C and then is held for 4 hours.

Catalyst characterization

A scanning electron microscope (SEM) was used to identify the surface morphology of the activated wood char catalyst. The surface area, pore size distribution and pore volume of activated wood char were measured using nitrogen physio sorption a Quantochrome Instruments Nova 3200e instrument. The specific surface area was calculated using a Brunauer–Emmett–Teller (BET) model for the nitrogen adsorption isotherm. The Barrett–Joyner–Halenda (BJH) adsorption model was used to determine the pore size of catalyst.

Experimental procedure

Hydro-cracking of Jatropha oil was done on micro fixed bed reactor with the activated carbon as bio-catalyst at atmospheric pressure condition. There are four variables used to assess catalyst activity. The variable temperature is 400^{o}C, 450^{o}C and 500^{o}C. The Jatropha oil flow rate is regulated using a syringe and manually injected with intervals of 2mL/5min, 2/10 and 2/15. The variance of hydrogen flow rates is 50 mL/min (STP). The concentration of hydrogen is also a concern in this study.

The configuration of reactor system is shown in Figure 1. Reactors made of stainless steel with an inner diameter of 1 cm and a height of 10 cm are filled with a catalyst of about 7 grams. Then the reactor containing the catalyst is heated to operating temperature at a heating rate of 5^{o}C/min. The reactor is purged using hydrogen or reactant for half an hour at operating temperature. Jatropha oil were injected into the reactor using a syringe at certain intervals. Cracking products are then cooled

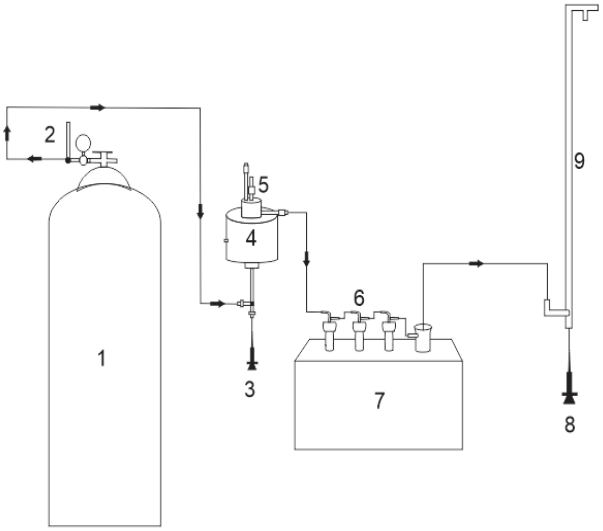


Figure 1. Schematic of apparatus for hydro-cracking process. (1) Cylinder of H_2 (2) Regulator (3) Syringe for feed (4) Electrical furnace (5) fixed bed reactor (6) Product collector (7) Ice bath (8) Syringe for soap (9) Bubble soap.

in a condenser system to get oil liquid products (OLP). Other products cannot be condensed in the condenser system and subsequently discharged into the environment without analysis. Non condensable gas is tested qualitatively using a flame test.

Data Collection

The bio-fuel obtained from hydro-cracking process were characterized by testing their density, kinematic viscosity, pH and chemical composition. Density was measured at room temperature using a container whose volume is known and calculated of the mass to the volume of the sample. Kinematic viscosity was determined using a Viscometer Ostwald at 25°C. The pH was use pH testing papers. The compositions of major chemical were analyzed using a Gas Chromatography–Mass Spectrometry (GC–MS).

$$Conversion\,(\%-wt)=\frac{m_{OLP}+m_G+m_{coke}}{m_{oil}}x100\% \quad (1)$$

$$Yield_{\,product}(\%-wt)=\frac{m_{product}}{m_{oil}}x100\% \quad (2)$$

where, m_{OLP} = mass of liquid product, m_G = mass of gas product, m_{coke} = mass of coke product and m_{oil} = mass of oil feed.

Performance parameters

The performance of the reaction was evaluated by using the conversion and yield parameters. The conversion and yield defined by equation (1) and (2), respectively.

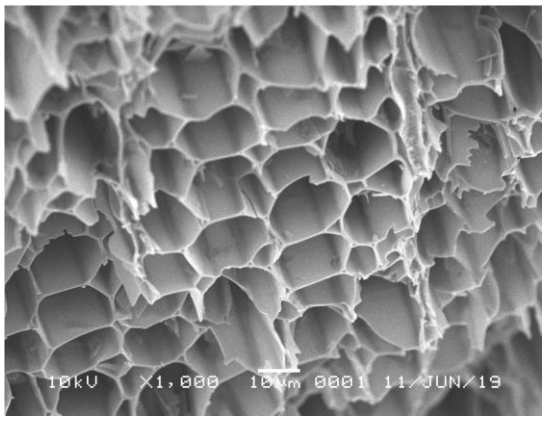
RESULTS AND DISCUSSION

Analysis of SEM (Scanning electron microscopy)

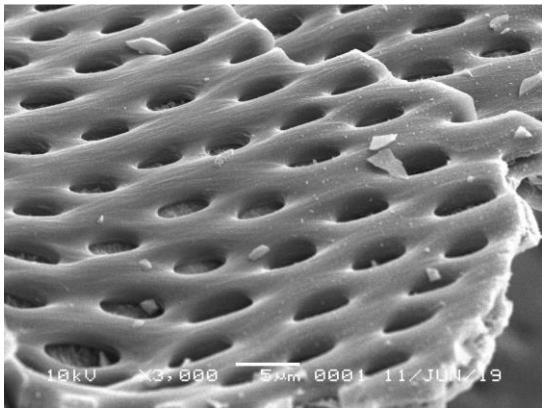
The surface morphologies of wood activated carbon is shown in Figure 2 with different scales. It appears that the structure of the activated wood char pores forms large holes with clean pore surfaces which are not filled by covering impurities. Then with a magnification of SEM 3000 times visible cavities are more structured, similar to the observation reported by Cheng and Li (2018).

Analysis of BET and BJH

Nitrogen adsorption-desorption was used for analysis of the pore structure and surface area of the catalyst. The curve of the N_2 adsorption-desorption is shown in Figure 3. From the data, at the relative pressure of 0.7-1.0, there was occurred slightly hysteresis during the desorption process, but this event is not clearly visible in the curve in Figure 3. Hysteresis occurs because at the same relative pressure, the number of nitrogen molecules that is desorbed shows a difference compared to the number of adsorbed nitrogen molecules. The hysteresis loop observed by the catalyst is a combination of micropores and mesopores. The micropore and mesoporous characteristics are shown by the pore size distribution data of the catalyst samples using the BJH method as shown in Figure 4. The catalyst samples showed that the



(a)



(b)

Figure 2. Images of SEM analysis of catalyst wood char: (a) 1000x magnification; (b) 3000x magnification.

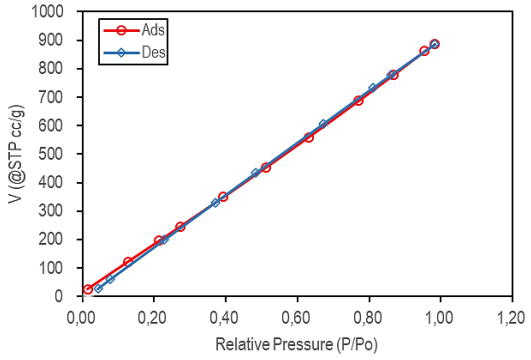


Figure 3. Isotherm adsorption and desorption of N_2.

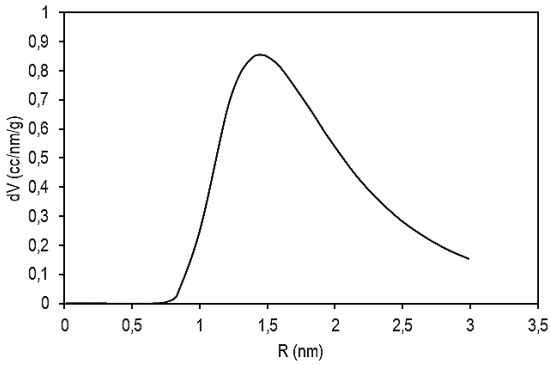


Figure 4. Pore size distribution using the BJH method.

micropores with a size below 2 nm had more numbers than the mesoporous size. The specific surface area was analyzed use BET model, where the surface area of catalyst was 1,301.2 m^2/g. The total pore volume of the pores and the average pore size was 1.37 cm^3/g and 21.1 A°, respectively. These results have a higher surface area and pore volume than the results of Januszewicz et. al. (2020) which were activated using KOH with a surface area of 1,194.4 m^2/g and a pore volume of 0.61 cm^3/g.

The yield of products and conversion

The yield of products and conversion of hydro-cracking Jatropha oil was shown in Table 3. Products obtained from the hydro-cracking process of Jatropha oil consist of oil liquid product, gas, coke and water. From hydro-cracking, the yield of oil liquid product increases with increasing operating temperature from 400 to 450°C, but the yield of oil liquid product decrease at 500°C. The suggested reaction temperature affects the yield of oil liquid product and it is inline to the Novia' study (2011). Feed liquid injection also affected to the yield of the oil liquid product. To study the effect of the feed liquid injection rate, it was taken at a temperature of 400°C. The oil liquid product increases as the feed injection rate decreases, this is due to increasing a residence time. Coke is always formed in every variation of the experiment. Coke is a product between intermediate cations which are more stable and accumulated in the catalyst during the reaction (Wijanarko et. al., 2006). The release of oxygen atoms present in the structure of Jatropha oil produces a water product. The highest oil conversion was obtained under operating conditions of 400°C temperature and feed injection rate of 2 ml/2minutes.

Physical properties

The physical properties of oil liquid products were measured as shown in Table 4. The Density has an important role in the atomization of fuel when the combustion (Urbán & Józsa, 2017). The densities of the reaction temperature 400°C and 500°C were almost the same, while for the reaction

Table 3. The yield of hydro-cracking products and Jatropha oil conversion.

Temperature (°C)	Liquid injection (ml/min)	Yield of (%-wt) OLP	Gas	Coke	Water	Conversion (%)
	2/2	39.0	49.3	9.8	1.8	98.2
400	2/5	46.0	37.8	13.1	3.1	96.9
	2/10	56.6	26.2	13.4	3.7	96.3
450	2/10	59.8	35.2	1.7	3.3	96.7
500	2/10	55.6	34.0	7.4	2.9	97.1

Table 4. Physical properties of oil liquid products.

Temperature (°C)	Liquid injection (mL/min)	Density^{25C} (g/cm^3)	Kinematic viscosity^{25C}(cSt)	Flash point (°C)	pH
400	2/2	0.859	4.838	28	5
	2/5	0.807	3.369	29	5
	2/10	0.869	4.266	24	5
450	2/10	0.730	1.090	22	5
500	2/10	0.877	2.859	20	5
gasoline		0.780	0.710	17	5
diesel*		0.836–0.850^{30C}	4-8^{30C}	45-60	-

*(Pramanik, 2003)

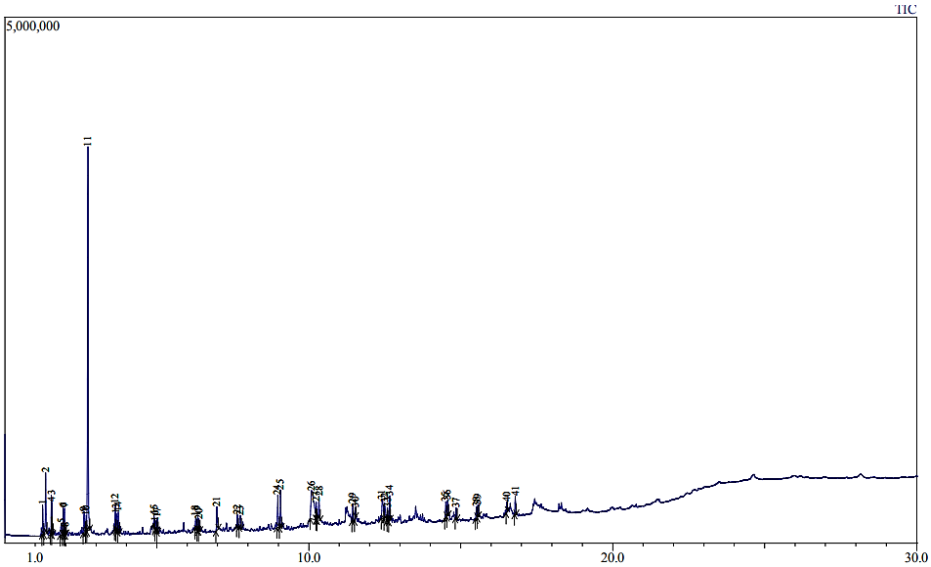


Figure 5. GC-MS Analysis of OLP at temperature 400°C and injection rate 2mL/10 min.

temperature 450°C the density is lower. It is also in line with the kinematic viscosity. This is because the temperature of 450°C produces compounds that have shorter chains.

The density tend to increase when the feed liquid injection rate enhanced. The chain of oil molecules is not completely cracked when the amount of oil being fed increases. Hence, in the product there are still long chain molecules which are indicated by a high density.

Based on the density and viscosity, the oil liquid product produced at temperatures of 400°C and 500°C is close to the properties of diesel fuel, where diesel fuel has a density of 0.836 - 0.850 g/cm^3 and a viscosity of 4-8 Cst. But for flash points below the commercial value of 40-55°C (Pramanik, 2003). For temperature of 450°C and injection rate of 2mL/10 min, the properties of OLP tend to be close to those of commercial gasoline.

Chemical properties

The GC-MS profiles of oil liquid products (OLP) from hydro-cracking process shown in Figure 5. The dominant chemical composition about 32.90%-mass of OLP was heptanal that assigned by the peak at retention time 2.736 min. The composition of the alkane group compound has an amount of 21.75% -mass. A total alkane group content from C_5 until C_{20}. Alkene compounds of 5.57% -mass consist of C_8 to C_{18}. The alkanone,

alkanol and alkanal compositions were 11.22, 2.94 and 35.9%-mass, respectively. Products of OLP also contain cyclic compounds of 12.28% -mass and 1.07% -mass aromatic compounds. A total of 9.28% -mass of unsaturated fatty acids is present in the product, this indicates that there are fatty acid compounds that have not been converted. Based on the product analysis, it shows that the activated wood charcoal used has the ability to cut the chain of jatropha oil molecules quite well.

CONCLUSION

A pore structure of wood char was used has a form like sieve with an average pore diameter of 21.1 A˚. The wood char catalyst is capable of producing a product consisting of OLP, water, gas and coke. The operating conditions, temperature and injection rate of the Jatropha oil feed have a significant effect on the conversion of castor oil and product yield. From all the operations that have been carried out, the highest oil liquid products were 59.80% -mass at a temperature of 450°C and a feed injection rate of 2 mL/10 min. Meanwhile, the highest conversion of Jatropha oil of 98.20% was obtained at a temperature of 400°C and a feed injection rate of 2 mL/2 min. The resulting OLP products contain alkanes, alkenes, alkanes, alkanes, alkanols, aromatics and unsaturated fatty acids.

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