THE EFFECT OF TEMPERATURE ON THE PERFORMANCE OF ACTIVATED CARBON OVER CATALYTIC CRACKING OF CRUDE PALM OIL

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Key Words	Abstract
Activated carbon, catalyst, catalytic cracking, crude palm oil	This research was carried out to investigate the effect of temperature in carbon production on its performance in the catalystic cracking of CPO to fuel. The carbon was produced using palm shell at 2 different temperatures (450 and 550ºC). The cracking of CPO was carried out with and without the active carbon catalyst. The result showed that the use of catalyst increase the conversion of both gas and liquid conversion. The use of higher temperature in the production of active carbon catalyst increased the performance of the catalyst, in particular, for the liquid conversion.

INTRODUCTION

Crude oil of fossil fuel balance in Indonesia shows a declining of crude oil production for about 4% per year, and in contrast a fuel consumption is incresing in average 4.7 % per year. If this situation still continue, it will change Indonesia status from crude oil exporter country to crude oil importer country in 2035 (Yudiartono et al., 2018). These facts had encouraged many scientists in Indonesia to search for the ways for efficient energy consumption along with the search for the new sources for fossil fuels and the researches for alternative renewable energy resources (Devita et al., 2017, Nazarudin et al., 2017)

For developing a renewable energy, Indonesian government released Presidential Decree No. 2 of 2006 about Nasional Energy Policy describing the principles of energy diversification, Furthermore, the Presidential Decree No.2 of 2015 about National Medium Term Development Plan (RPJMN) stated the strategic poilicies of science and technology development including strategy of renewable energy. This policy emphasizes the use of alternatives energy such as plant-based fuels which is highly potential in Indonesia. (Devita et al., 2017, Nazarudin et al., 2017). Indonesia is the largest producer of crude palm oil in the world. The production of CPO in Indonesia was expected to reach at 40.5 million tons in 2018/2019, that grows approximately five percent from 2017/2018. Therefore, crude palm oil is one of some potential sources for plant based fuels which can be developed in Indonesia (Elst, 2018, McDonald and Rahmanulloh, 2018, Rafiie, 2018).

The high amount of CPO production in Indonesia has caused the high amount of waste produced in the factory. According to previous research, generally the solid waste produced from palm oil mill is empty bunch (24-35%). The utility of this waste has not optimally done. Nowadays, about 70% of solid waste is utilised by burning them to produce heat for boiler. This utilisation has produced charcoal and ash which are abundant. It is not like the ash which has been used for organic fertilizer, the carbon has not been utilised(Nazarudin et al., 2017).

The solid waste can be converted to activated carbon by combination of chemical and physical (calcination) treatment that can improve the physical and chemical properties of the material. A activated carbon in the form of granuluar and powder has a large pores which are a good for absorbency, catalyst, and catalyst support (Luangkiattikhun, 2007, Nazarudin et al., 2017, Rugayah et al., 2014). Metal-embedded catalyst such as Cr-Carbon and Ni- Carbon has many advantages where the active metals were better dispersed compare to those unembedded due to the increase in surface area of active site in metal catalyst(Nazarudin et al., 2017). However, the process to embed the metal into the catalyst requires some spaces in term of catalyst pores(Wan and Hameed, 2011, Thushari and Babel, 2018). This current research was undergone to investigate the use of temperature in the activation of carbon as a process that can be used to increase the surface area of catalyst pores and in turn affects its performance in catalytic cracking of CPO to gasoline.

METHODS

The Production of Carbon and Activation of Carbon Catalyst

The production of carbon was done by burning palm shells in the batch reactor at 450 and 550°C without enough amount of oxygen. The activation of carbon was carried out chemically by using NaOH. Some amount of carbon was mixed using NaOH pellet and distilled water with ratio carbon:distilled water:NaOH was 1:3:1. This mixtures was stirred continously for 2 hours at 40°C. The carbon was filtrated and washed. The carbon was then redissolved in CH$_3$COOH 25% for 30

minutes and refiltrated. This procedures was repeated until the acid solution turned netral (pH=7). The carbon was dried in the dryer at 105°C for 4 hours.

Characterization of Catalyst

The characterization was done by *X-ray diffraction* (XRD) and *Scanning Electron Microscope* (SEM).

The Thermal and Catalytic Cracking

There were 2 cracking process done in the current research: thermal cracking and catalytic cracking. Thermal cracking was carried out as comparison to those with catalysts. Similar process were done for both cracking process except for the use of active carbon in the vertical furnace at catalytic cracking process. The cracking was carried out by using ratio of catalyst to *crude palm oil* (CPO) 1: 10. Length of cracking was 1 hour with cracking reactor temperature was 723 K and horizontal furnace (gasification reactor) at 673 K.

CPO sample was injected to heated horizontal reactor. CPO flowed to vertical furnace and underwent heating to produce liquid yield which further being collected and weighed. Total solid residu was also weighed which consist of catalyst residu and cocass.

Gravimetric Analysis

Gravimetric analysis was carried out for cracking products: gases, liquid, cocass, and CPO residu. This analysis was done to calculate conversion for each cracking product (gasoline, diesel) and conversion ratio (gas + liquid)/cocass which was symbolised as H/K (Nazarudin, 2000).

a. % cracking product $= \frac{weigh\ cracking\ product}{weigh\ feed}$ x 100%

b. % total conversion $= (1- \frac{weigh\ feed\ residue}{weigh\ feed})$ x 100%

c. H/K $= \frac{liquid\ conversion+gas\ conversion)}{cocass\ conversion}$

d. % residue $= \frac{Weigh\ feed\ residue}{weigh\ feed}$

Gas Chromatography– Mass Spectroscopy (GC-MS)

Liquid produced during cracking was analysed using GC-MS to obtain type of hydrocarbon produced (qualitative) and the number of hydrocarbon in the liquid (quantitative). The operation condition for GC-MS can be seen at Table 1.

Table 1. Operation condition for GC-MS

Parameter	Condition
Temperature oven 1	40ºC
Time Isothermal 1	10
Increase of Temperature	5ºC/menit
Temperature oven 2	270ºC
Sensitiviy FID	Low
Detector	On
Temperature Detector	300ºC
Gas Carrier	Helium, 10 Kpa
Injection	0,2µl
Temperature Injector	270ºC
Time	75 minutes

RESULT AND DISCUSSION

Active Carbon Catalyst

The use of different temperature in the production of active carbon catalyst has affected the crystallinity of catalyst produced. As shown in Fig 1 below, result from XRD showed the active carbon catalyst produced using 450ºC has less crystallinity compare to active carbon catalyst produced using 550ºC. The increase in the crystallinity of active carbon was as expected since it exhibits similar form of crystal catalyst. The uniformity of crystal catalyst can be used to predict the product of catalytic process more easily.

SEM images (Fig 2) confirmed that the use of higher temperature in the production of active carbon catalyst has removes the impurities present in the carbon. The result showed that the use of higher temperature (550ºC) gives better sites for metal to be embedded in the active carbon to increase its performance in the catalytic cracking.

Catalytic Cracking

The result of cracking of CPO is shown in Table 2. This result showed that the use of active carbon as catalyst increased both gas and liquid conversion. This result also showed that the use of active carbon catalyst has better performance in liquid conversion if it is produced at higher temperature (550ºC). At lower temperature (450ºC), active carbon catalyst produced less liquid and more gas.

As shown in Fig 2 and Fig 3, the chromatogram for liquid produced by both catalyst are similar, however, the compound present in the liquid as shown in Table 3 and Table 4 are actually different.
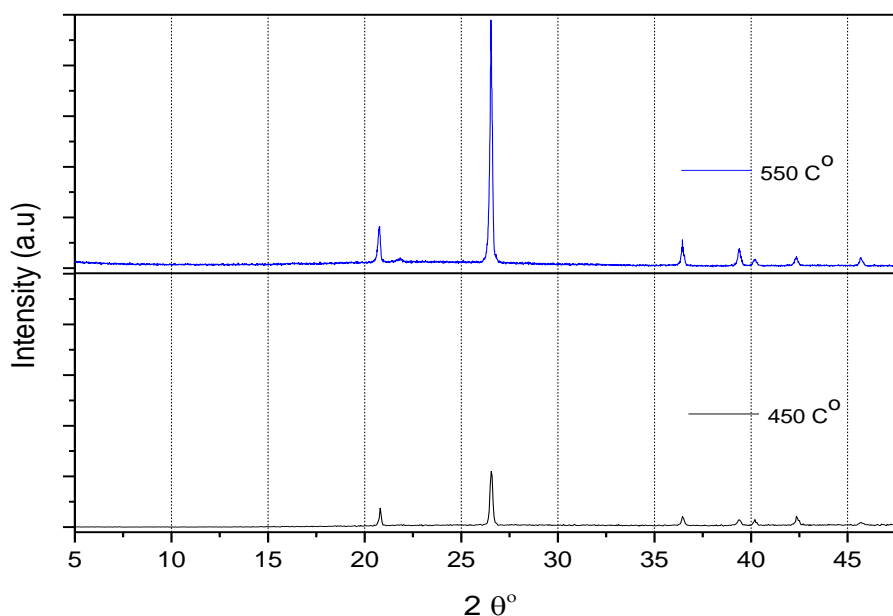

Fig 1. XRD pattern of active carbon catalyst produced using 2 different temperatures: 450ºC (below) and 550ºC (top)

a   **b**
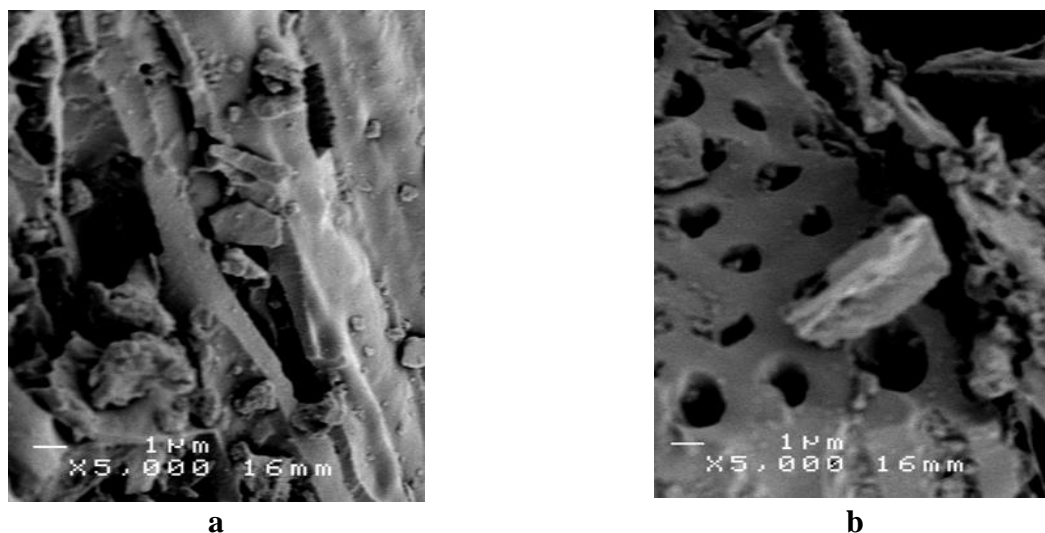
Fig 2. SEM Images of active carbon catalyst produced using 2 different temperatures: 450ºC (a) and 550ºC (b)

Table 2. The product of thermal and catalytic cracking of CPO at 500ºC

Cracking	Conversion (%)		
	Liquid	Gas	Coke
Thermal cracking	2	3	0
Catalytic cracking using active carbon catalyst produced at 450ºC	79	20	1
Catalytic cracking using active carbon catalyst produced at 550ºC	85	14	1
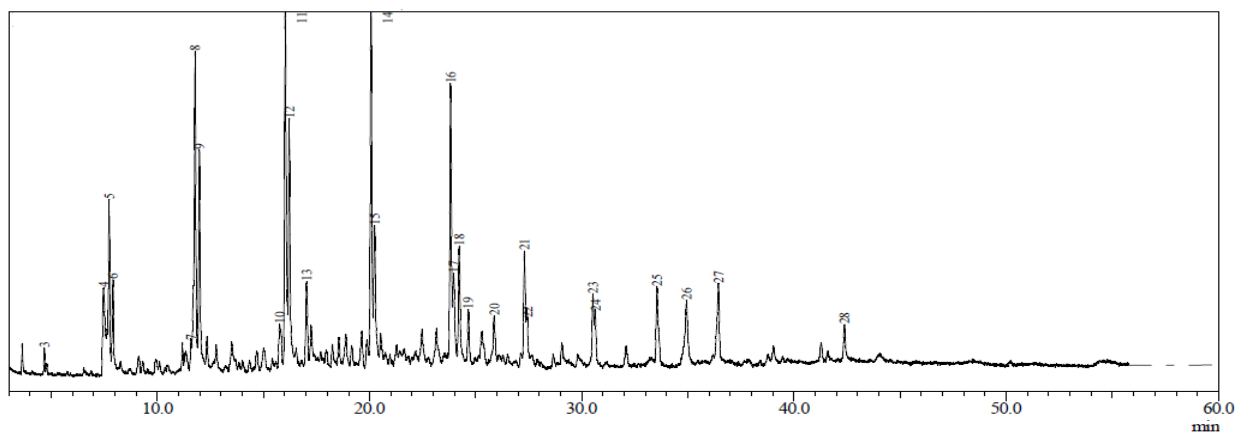
Fig 3. Chromatogram GC for liquid produced by catalytic cracking of CPO using active carbon catalyst produced at 450ºC , cracking temperatur 500 ºC

Fig 4. Chromatogram GC for liquid produced by catalytic cracking of CPO using active carbon catalyst produced at 550ºC , cracking temperatur 500 ºC

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Table 3. The compound in the liquid product of cracking using active carbon catalyst produced at 450°C
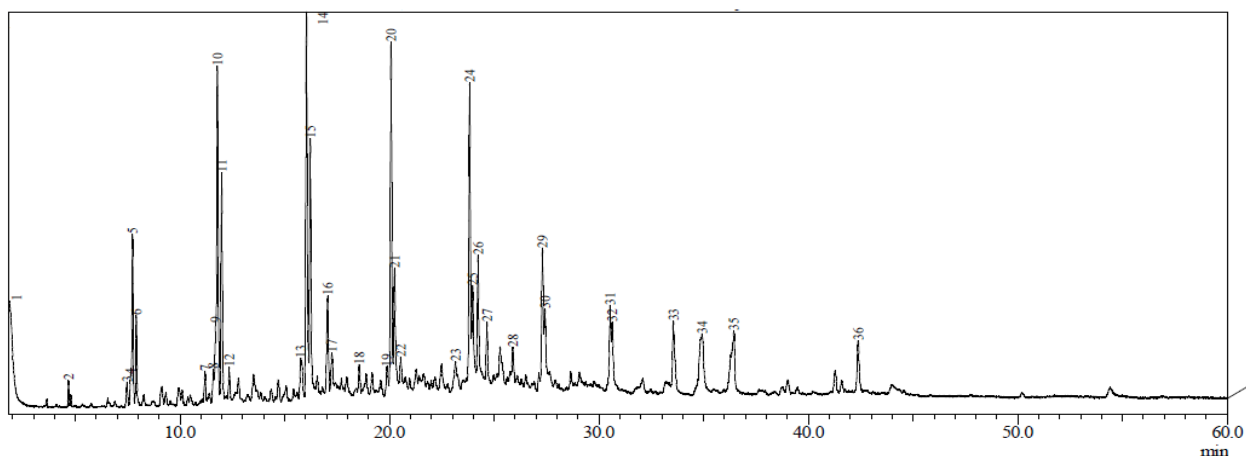
No.	RT	% Area	SI*	Compound Name	Molecular Formula	Molecular Weight
1.	2.308	0.41	60	*3-Tridecen-1-yne, (Z)*	$C_{13}H_{22}$	178
				Verbenol	$C_{10}H_{16}O$	152
2.	2.606	32.05	90	*Methylamine*	CH_3D_2N	31
3.	7.470	6.05	94	*Acetic acid*	$C_2H_4O_2$	60
4.	7.739	3.30	96	*1-Heptene*	C_7H_{14}	98
				Cyclobutane, isopropyl	C_7H_{14}	98
5.	7.916	1.20	95	*Heptane*	C_7H_{16}	100
6.	11.700	0.98	97	*Benzene, methyl*	C_7H_8	92
				Toluene	C_7H_8	92
7.	11.786	4.38	96	*1-Octene*	C_8H_{16}	112
8.	11.993	3.09	92	*Heptane, 2,4-dimethyl*	C_9H_{20}	128
9.	15.758	0.67	88	*Benzene, ethyl*	C_8H_{10}	106
10.	16.034	6.52	96	*1-Nonene*	C_9H_{18}	126
11.	16.224	3.95	96	*Nonane*	C_9H_{20}	128
12.	17.048	1.23	93	*Bicyclo 5.1.0 octane*	C_8H_{14}	110
				Cyclooctene, (Z)	C_8H_{14}	110
13.	17.290	2.70	95	*1,3,5,7-Cyclooctatetraene*	C_8H_8	104
14.	18.884	0.53	84	*Hexanoic acid*	$C_6H_{12}O_2$	116
15.	20.072	6.54	96	*1-Decene*	$C_{10}H_{20}$	140
16.	20.240	1.85	95	*Decane*	$C_{10}H_{22}$	142
17.	23.824	6.49	93	*1-Undecanol*	$C_{11}H_{24}O$	172
				1-Undecene	$C_{11}H_{22}$	154
				1-Tridecene	$C_{13}H_{26}$	182
18.	23.962	1.81	94	*Undecene*	$C_{11}H_{24}$	156
19.	24.225	2.63	94	*5-Undecene*	$C_{11}H_{22}$	154
20.	24.659	1.18	91	*Cyclopropane, nonyl*	$C_{12}H_{24}$	168
				1-Decene	$C_{10}H_{20}$	140
				1-Undecanol	$C_{11}H_{24}O$	172
21.	25.876	0.99	94	*Heptanoic acid*	$C_7H_{14}O_2$	130
22.	27.299	2.96	94	*Cyclododecane*	$C_{12}H_{24}$	168
				1-Dodecanol	$C_{12}H_{26}O$	186
				1-Tridecene	$C_{13}H_{26}$	182
23.	27.418	1.15	92	*N-Tetradecane*	$C_{14}H_{30}$	198
				Nonane, 3-methyl-5-propyl	$C_{13}H_{28}$	184
				Nonane, 2-methyl-5-propyl	$C_{13}H_{28}$	184
24.	30.527	1.86	89	*1-Dodecanol*	$C_{12}H_{26}O$	186
				Cyclododecane	$C_{12}H_{24}$	168
				1-Tridecene	$C_{13}H_{26}$	182
25.	30.642	1.41	91	*Tridecane*	$C_{13}H_{28}$	184
				N-Tetradecane	$C_{14}H_{30}$	198
				Nonane, 2-methyl-5-propyl	$C_{13}H_{28}$	184
				Pentadecane	$C_{15}H_{32}$	212
26.	33.556	2.11	91	*Cyclododecane*	$C_{12}H_{24}$	168
				1-Dodecanol	$C_{12}H_{26}O$	186
27.	33.658	0.48	67	*Benzene, (2,3-dimethyldecyl)*	$C_{18}H_{30}$	246
28.	36.437	1.49	94	*N-Tetradecane*	$C_{14}H_{30}$	198

*: similarity index

Table 4. The compound in the liquid product of cracking using active carbon catalyst produced at 550°C

No.	RT	% Area	SI	Compound Name	Molecular Formula	Molecular Weight
1	1.851	1.25	84	OKTADECANE, 1-CHLORO	C18 H37 CL	288
				HEXADECANE, 1-CHLORO	C16 H33 CL	260
				DODECANE, 1,2-DIBROMO	C12 H24Br2	326
				1-Tetracosanol	C24 H50 O	354
2	4.678	0.43	95	1-Hexene	C6 H12	84
3	7.465	0.41	91	Benzene	C6 H6	78

No.	RT	% Area	SI	Compound Name	Molecular Formula	Molecular Weight
4	7.633	0.67	92	Cyclobutane, ethenyl	C6H10	82
5	7.735	3.99	96	1-Heptene	C7 H14	98
6	7.914	2.04	96	HEPTANE	C7 H16	100
7	11.189	0.61	94	Cyclohexene, 3-methyl	C7 H12	96
8	11.592	0.77	93	Bicyclo [5.1.0] octane	C8 H14	110
9	11.700	1.64	98	Benzene, methyl	C7 H8	92
10	11.786	8.90	97	1-Octene	C8H16	112
11	11.989	6.07	92	Heptane, 2,4-dimethyl	C9H20	128
				Octane	C8H18	114
12	12.351	0.62	95	2-Octene	C8 H16	112
13	15.764	1.89	83	Benzene, ethyl	C8 H10	106
14	16.037	10.83	96	1-Nonene	9H18	126
				Cyclopropane, octyl	C1 1H22	154
15	16.224	6.34	97	Nonane	C9H20	128
16	17.048	2.94	95	Cyclooctene	C8H14	110
17	17.246	1.11	90	Benzene, 1,2-dimethyl	C8 H10	106
18	18.554	0.69	87	Pentalene, octahydro-1-methyl	C9H16	124
19	19.875	0.74	74	Bicyclo 3.1.1 heptan-2-one, 6,6-dimethyl	C9H14O	138
				Hi-oleic safflower oil	C21 H22 O11	450
20	20.075	9.88	96	1-Decene	C10H20	140
21	20.244	3.79	95	Decane	C10H22	142
22	20.534	0.83	92	2-Decene	C10H20	140
23	23.157	0.24	80	Bicyclo (2.2.1)-5-heptene-2-carboxaldehyde	C8H10O	122
24	23.830	8.40	93	1-Undecene	C11H22	154
				1-Undecanol	C1 1H24O	172
25	23.974	2.95	95	UNDECANE	C11 H24	156
26	24.226	3.03	93	5-Undecene	C11H22	154
				Cyclopropane, nonyl	C12H24	168
				5-Tetradecene	C14 H28	196
27	24.657	1.48	92	Cyclopropane, nonyl	C12H24	168
				1-Decene	C10H20	140
				Cyclopropane, octyl	C1 1H22	154
28	25.889	0.79	91	heptanoic acid	C7 H14 O2	130
29	27.306	3.90	95	Cyclododecane	C12 H24	168
				1-Undecanol	C1 1H24O	172
30	27.419	1.66	93	Decane, 2,3,5-trimethyl	C13 H28	184
				N-TETRADECANE	C14 H30	198
				Dodecane	C12 H26	170
				TRIDECANE	C13 H28	184
31	30.531	2.13	91	1-Dodecanol	C12H26O	186
				Cyclododecane	C12 H24	168
32	30.631	1.71	93	Nonane, 2-methyl-5-propyl	C13H28	184
33	33.556	2.41	96	1-Pentadecene	C15H30	210
34	34.918	2.81	91	DECANOIC ACID	C10 H20 O2	172
35	36.437	0.48	92	Pentadecane	C15H32	212
				Nonane, 3-methyl-5-propyl	C13H28	184
				Heptadecane	C17H36	240
				N-TETRADECANE	C14 H30	198
36	42.379	1.60	88	acrylic acid tetradecanyl ester	C17 H32 O2	268

CONCLUSION

Solid waste from palm oil mill such as palm shell can be used to produce active carbon catalyst. Active carbon catalyst increased the conversion of both gas and liquid conversion in the catalytic cracking of CPO compare to thermal cracking. The use of higher temperature in the production of active carbon catalyst increased liquid conversion in the catalytic cracking of CPO

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