

## Thermo-catalytic decomposition of waste lubricating oil over carbon catalyst

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**Abstract**—The thermo-catalytic decomposition of waste lubricating oil over a carbon catalyst was investigated in an I.D. of 14.5 mm and length of 640 mm quartz tube reactor. The carbon catalysts were activated carbon and rubber grade carbon blacks. The decomposition products of waste lubricating oil were hydrogen, methane, and ethylene in a gas phase, carbon in a solid phase and naphthalene in a liquid phase occurring within the temperature ranges of 700 °C–850 °C. The thermo-catalytic decomposition showed higher hydrogen yield and lower methane yield than that of a non-catalytic decomposition. The carbon black catalyst showed higher hydrogen yield than the activated carbon catalyst and maintained constant catalytic activity for hydrogen production, while activated carbon catalyst showed a deactivation in catalytic activity for hydrogen production. As the operating temperature increased from 700 °C to 800 °C, the hydrogen yield increased and was particularly higher with carbon black catalyst than activated carbon. As a result, carbon black catalyst was found to be an effective catalyst for the decomposition of waste lubricating oil into valuable chemicals such as hydrogen and methane.

Keywords: Catalytic Decomposition, Waste Lubricating Oil, Carbon Black, Hydrogen

### INTRODUCTION

Hydrogen, recognized as an efficient and sustainable source of energy and one of the most important base materials in the chemical industry, is mainly used for the production of methanol and ammonia and in the process of petroleum refinement [1]. In principle, hydrogen can be produced from hydrocarbon fuels by steam methane reforming, partial oxidation, auto-thermal reforming, and direct decomposition of methane. Currently, the largest and most economical method of hydrogen production is steam reforming of methane. However, it has been generally acknowledged that the emission of CO<sub>2</sub> from the steam reforming of methane causes greenhouse effects, which should be avoided. Clean production of hydrogen, e.g., from methane by plasma [2] and from reduction-oxidation of metal oxides [3], is not competitive with current energy costs or practically efficient. The catalytic decomposition of hydrocarbons into hydrogen and carbon is an alternative, single process to produce hydrogen of necessary purity. A kinetic study of methane decomposition on carbonaceous catalysts and transition metals has been conducted [4–6]. Shah et al. [4,7] examined nano-scale binary, Fe-based catalysts for catalytic dehydrogenation of light alkanes at low temperature. This process showed promising activity at the beginning of the reaction; however, rapid catalyst deactivation occurred at high temperatures due to the carbon deposited on the catalyst and the need for an additional catalyst regeneration process. Regeneration of those catalysts by combustion of carbon deposits resulted in the production of a large amount of CO<sub>2</sub>. When carbonaceous catalysts are used, their regeneration via re-

moval of the produced carbon is not necessary. Among these carbonaceous catalysts, activated carbon and carbon black have shown reasonable activity and stability for the decomposition of various hydrocarbons [5,6].

The decomposition of liquid hydrocarbon over carbonaceous catalysts and transition metals has also been investigated. Muradov et al. [8] examined the decomposition of gasoline over activated carbon, and Wang et al. [9] and Takenaka et al. [10] investigated the decomposition of cyclohexane and kerosene over transition metals. Currently, waste lubricating oil (WLO) is used for fuel oil or for reuse after refinement. Permsubscul et al. [11] investigated the catalytic cracking of waste lubricating oil into liquid fuels. Similarly, Lazaro et al. [12] investigated the production of hydrogen from mineral waste oil by thermo-catalytic decomposition. In the thermal decomposition of waste lubricating oil (WLO), it was expected that at temperatures of 700–850 °C, the long chain hydrocarbon of lubricating oil (average carbon number C<sub>14</sub>) decomposed into shorter chains of hydrocarbon such as methane, ethylene, ethane, propane, and butane. Furthermore from previous studies conducted in our laboratory concerning the thermo-catalytic decomposition of methane [5,6,13,14], ethane [15], propane [16], and butane [17] over carbon catalysts, the catalytic activity of carbon black and activated carbon for the production of hydrogen, carbon, and methane was observed. In particular, the carbon black catalyst showed constant catalytic activity without any deactivation during carbon deposition. The advantage of the carbon black catalyst over a metal catalyst is that there is no deactivation of catalyst due to carbon coking in the course of the decomposition of hydrocarbon. Both carbon black and the produced carbon during the thermo-catalytic decomposition of hydrocarbon deposited on the active site of carbon black catalyst act as new active sites, thus maintaining catalytic activity in spite of carbon deposition. Further details concerning

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this phenomenon can be found elsewhere [18]. Therefore, we expected that the thermal decomposition of waste lubricating oil of average carbon number of  $C_{14}$  produced shorter hydrocarbons such as methane, ethylene, ethane, propane, and butane, and after the thermo-catalytic decomposition of these short hydrocarbons valuable chemicals such as hydrogen and methane would be produced with the aid of the carbon black catalyst without catalytic deactivation. In fact, the objective of this study was to extend the catalytic activity of the carbon catalyst to liquid hydrocarbon such as waste lubricating oils, while examining the catalytic action of the carbon catalyst for the thermo-catalytic decomposition of long and short chain hydrocarbons from the product gas yield of hydrogen and methane.

## EXPERIMENTAL

### 1. Reagents

The raw material in this study was waste lubricating oil. Commercial lubricating oil was made from a mixture of lubricant base oil and additives, and the additives were determined by the intended application of the lubricating oil. In this study, the waste lubricating oil was supplied by an aluminum rolling process from a domestic company. The composition of the employed sample was analyzed using gas chromatography and mass spectroscopy, with the results given in Table 1. From the mass spectroscopy results of waste lubricating oils, the average molecular form of the waste lubricating oil was estimated to be  $C_{14.3}H_{30.3}$ . The physical properties of the employed carbon catalysts are presented in Table 2. The  $N_2$  BET specific surface area of the carbon blacks was  $82 \text{ m}^2/\text{g}$ , and that of the activated carbon was  $1,071 \text{ m}^2/\text{g}$ . The carbon catalyst samples were dried at  $200^\circ\text{C}$  for 24 hr in air before the experiment.

### 2. Experimental Setup

Experiments were conducted in a fixed-bed quartz reactor of 14.5 mm I.D. and 640 mm in length and placed in an electric fur-

**Table 1. Composition of waste lubricating oil (WLO) by GC-MS**

Waste lubricating oil (WLO)	%
Tridecane	18.8
Tetradecane	29.3
Pentadecane	5.0
Distillates (methyl-decane, methyl-propyl-cyclohexane, pentyl-cyclohexane, etc.)	46.9

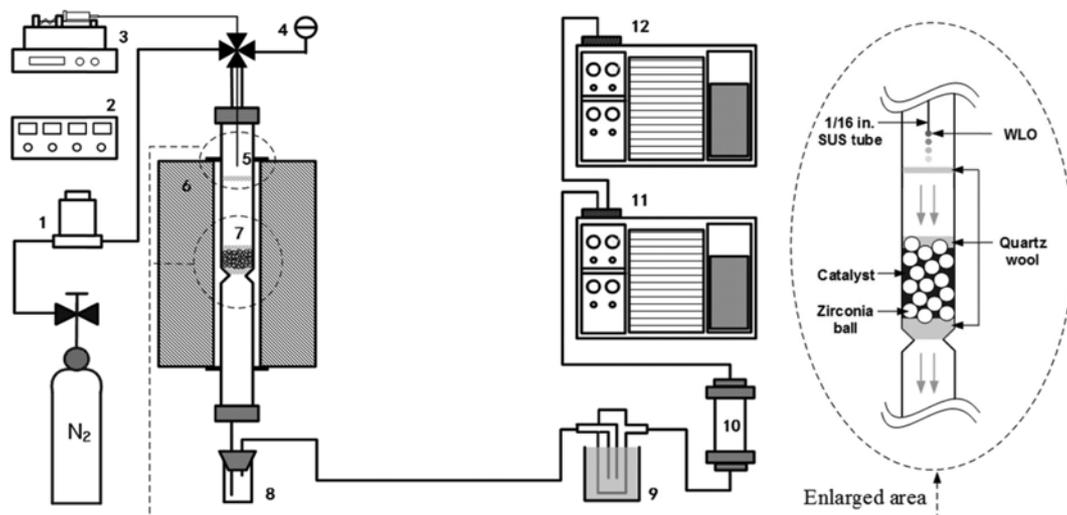
Average molecular formula:  $C_{14.3}H_{30.3}$

Average molecular weight:  $212.6 \text{ g/mol}$

**Table 2. Properties of employed carbon catalysts**

Carbonaceous catalysts	Particle size	Surface area
Activated carbon (from coconut)	$1140 \mu\text{m}$	$1071 \text{ m}^2/\text{g}$
Rubber black (N330)	$30 \text{ nm}$	$82 \text{ m}^2/\text{g}$

nace as shown in Fig. 1. The waste lubricating oil was injected into the reactor with a syringe pump through a 1/16 in stainless steel tube and evaporated at the outlet of the tube. Nitrogen gas as a diluent was also injected into the reactor with an MFC, and a mixture of oil vapor and nitrogen then entered the reactor. The reactor wall temperature was controlled via a K-type thermocouple placed on the outer reactor wall. The temperature of the furnace was determined by the calibration data between the temperature of the catalyst bed and the reactor wall. The quartz tube was narrowed somewhat in the middle, and rock wool was placed there to support the catalyst particles. The catalyst sample was packed between rock wool in the middle of the reactor. The reaction condition was the catalyst loadings of 0.2 g for standard loading and 0.4 g for comparison and the reactant mass flow rate was  $0.015 \text{ g min}^{-1}$ , and the purge nitrogen volume flow rate was  $9.25 \text{ cm}^3/\text{min}$  (STP). After the desired temperature was obtained while the reac-



**Fig. 1. Schematic diagram of the experimental facility.**

1. Mass flow controller (MFC)

2. MFC control box

3. Liquid pump

4. Pressure gauge

5. 1/16 in. SUS tube (WLO inlet)

6. Electric tube furnace

7. Catalyst

8. Liquid trap

9. Cold trap

10. Filter

11. GC (Ar carrier)

12. GC (He carrier)

tor was purged with nitrogen, the reaction experiment was started by injecting the waste lubricating oil. The feeding time of waste lubricating oil was 120 min. During experiments the gas phase products were analyzed using two gas chromatographs in series equipped with a thermal conductivity detector (TCD). The first gas chromatograph was equipped with a Carboxen 1006 column (Supelco) with argon carrier gas, and the second chromatograph was equipped with a Haysep Q column with helium carrier gas.

## RESULTS AND DISCUSSION

### 1. Non-catalytic Thermal Decomposition

A non-catalytic thermal decomposition experiment was conducted to compare the catalytic activity of carbon catalysts in the range of 700 °C-800 °C. Fig. 2 shows the gas production rate as a function of time at 750 °C from which methane, ethylene, and hydrogen were produced. During the two hour decomposition reaction, the time average product gases were as follows: methane production of 2.7-2.8 mole/mole WLO, ethylene production of 1.7-1.8 mole/mole WLO, and hydrogen production of 0.8 mole/mole WLO, respectively. Table 3 displays the product gas composition under different operating temperatures. Since thermo-catalytic decomposition of waste lubricating oil favored higher temperatures for greater methane and hydrogen production, small amounts of  $C_2H_6$ ,  $C_3H_8$ , and  $C_{4+}$  were neglected in the analysis of product gas composition for simplicity.

As shown in Fig. 2, most of the decomposition products were ethylene, methane, and hydrogen. Since hydrogen was produced, it was confirmed that solid carbon was also produced, and from previous research of the thermo-catalytic decomposition of methane, ethane, propane and butane, it was found that this produced

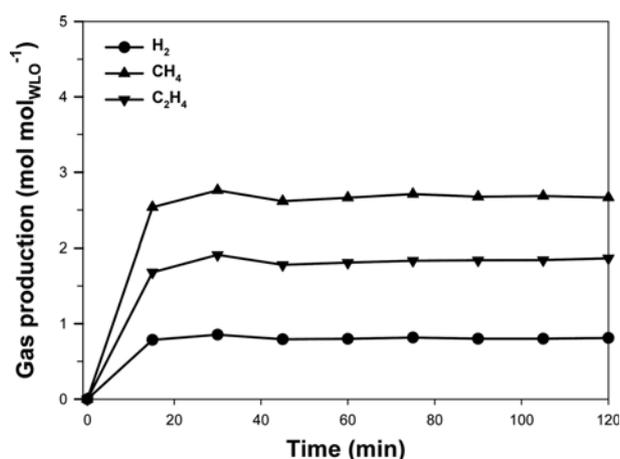


Fig. 2. Gas production rate under non-catalytic reaction at 750 °C.

Table 3. Material balance of product distribution at 800 °C (catalyst loading: 0.2 g)

	Gas (%wt)	Solid (%wt)	Liquid (%wt)
Non-catalytic	64.83	8.66	26.51
Activated carbon	70.04	13.41	16.55
Carbon black	81.11	11.76	7.13

carbon could act as a carbon catalyst.

After the experiment some dark-colored liquid phase products were found at the reactor wall and cold trap. From the mass spectroscopy analysis of the liquid product, most of the products were naphthalene and naphthalene derivatives (phenanthrene, ethylbenzene, pyrene, biphenylene, etc.), while the rest were un-reacted-waste lubricating oils (dodecane, tridecane).

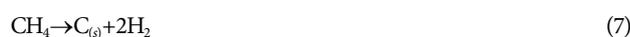
Since the thermal degradation of organic materials was composed of multiple series and parallel reactions [19], it was very difficult to identify the mechanism of decomposition and formation of each chemical. Thus, simple and well known chemical reactions were proposed and analysis was conducted.

Waste lubricating oils are composed of tridecane, tetradecane, pentadecane and derivatives of decane. Several olefins were formed in the primary cracking reaction, which undergoes a much greater number of parallel and consecutive reactions than does the product paraffin. Olefins which have a chain length of six or more carbons are quickly cracked, whereas the  $C_4$  and  $C_5$  olefins react to form greater molecular weight materials, aromatics and coke [20].

Let us suppose butane or propane were the light hydrocarbons. Olefin produced in the first step of decomposition of the lubricating oil has a chain length of around six, and olefin which has a chain length of six or more is quickly cracked, thereby producing butane and propane. Yoon et al. [17] and Muradov [21] found that product gases from the decomposition of butane are propane, propylene, ethane, ethylene, methane and hydrogen. Primary butane decomposition occurs by reactions (1) and (2) below. Since the C-C bond is much weaker than the C-H bond, the primary products of the light hydrocarbons will be the lower hydrocarbons from the C-C bond rupture. It is already known that during the thermal cracking of linear hydrocarbon, reaction (1) occurs more frequently than reaction (2) [22].



Furthermore, propylene, ethylene and ethane produced from primary butane decomposition were decomposed into methane and hydrogen. Propylene and ethane were further decomposed into ethylene or methane and eventually into hydrogen and carbon as the reaction temperature increased [15,17]. The possible decomposition reactions of propylene, ethane, ethylene and methane are shown in Eqs. (3), (4), (5), (6), and (7), and it is expected that major decomposition products are hydrogen, methane, ethylene and solid carbon.



### 2. Catalytic Decomposition over Activated Carbon and Carbon Black

The production rates of methane, ethylene, and hydrogen from

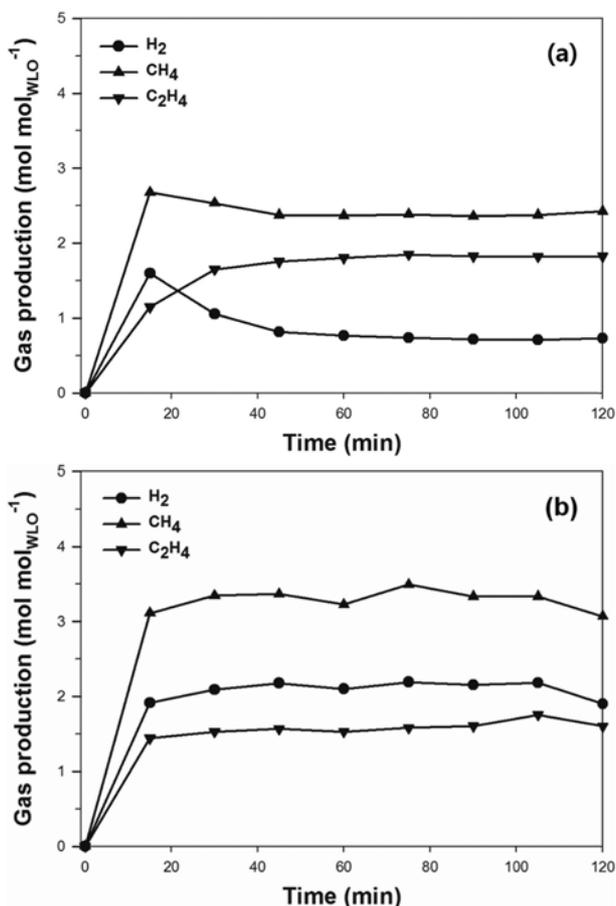


Fig. 3. Gas production rates over (a) activated carbon and (b) carbon black at 750 °C.

the thermo-catalytic decomposition of WLO over activated carbon and carbon black at a temperature of 750 °C are given in Fig. 3(a) for activated carbon and Fig. 3(b) for the carbon black catalyst. The production rates of product gases as a function of time showed a different pattern compared with non-catalytic decomposition. As shown in Fig. 3(a) for the activated carbon catalyst, the hydrogen production rate reached 1.5 mol/mol WLO and then decreased with time to a constant production rate of 0.8 mol/mol WLO, which was the same hydrogen production rate obtained in the non-catalytic case. The production rates of methane and ethylene were almost the same as those obtained from the non-catalytic condition. These decreased hydrogen production rates resulted from the coking of the deposited carbon during the decomposition of methane and ethylene into hydrogen and carbon. Since the produced carbon deposited in the pore of the activated carbon, the surface area of the activated carbon decreased. After experiment the surface area of activated carbon was reduced to 80 m<sup>2</sup>/g, and this significant reduction caused the deactivation of activated carbon in the production of hydrogen and carbon. However, in the case of the carbon black catalyst, the production rates of methane, ethylene, and hydrogen differed from those of the activated carbon catalyst and non-catalytic conditions. First, the hydrogen production rate was in the range of 2.0-2.2 mol/mol WLO and was higher than that of activated carbon and non-catalytic condi-

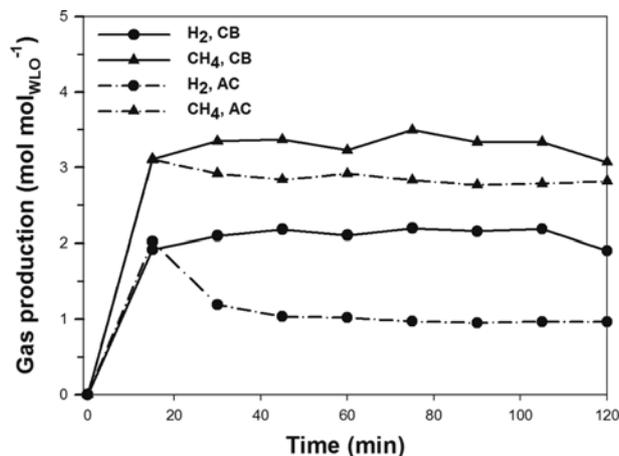


Fig. 4. Comparison of gas production over activated carbon and carbon black at 750 °C.

tions. Also, the production rate of hydrogen was greater than that of ethylene. However, in the case of the activated carbon catalyst and non-catalytic conditions, ethylene production was greater than hydrogen production. From this result it can be determined that the carbon black catalyst is an effective catalyst in the production of hydrogen and carbon from ethylene and methane. Additionally, from the greater methane production rate of 3.2-3.5 mol/mol WLO over the carbon black catalyst, one may also conclude that the carbon black catalyst was effective in the production of methane, as well as hydrogen from the waste lubricating oils. A comparison of production rates of methane and hydrogen as a function of time with activated carbon and the carbon black catalyst is shown in Fig. 4. As shown in Fig. 3, the activated carbon catalyst hydrogen production rate decreased with time and the methane production rate was constant with time. Therefore, the deactivation of activated carbon resulted from carbon deposition during the production of hydrogen and carbon from methane, ethylene and so on. In the case of the carbon black catalyst, production rates of hydrogen and methane were constant with time and production rates of both gases were higher than that of the activated carbon catalyst. The constant numbers of active sites allowed for constant catalytic activity of the carbon black catalyst and can explain the constant production rates of hydrogen. From Fig. 4, it was also determined that the difference in production rates of hydrogen between the activated carbon and carbon black catalyst was larger than that of production rate of methane. This implies that the carbon black catalyst was more effective in the production of hydrogen than methane from the thermo-catalytic decomposition of WLO. The comparison of production rates of hydrogen and methane with the carbon black catalyst and without catalyst is shown in Fig. 5. The production rates of methane and hydrogen with the carbon black catalyst were

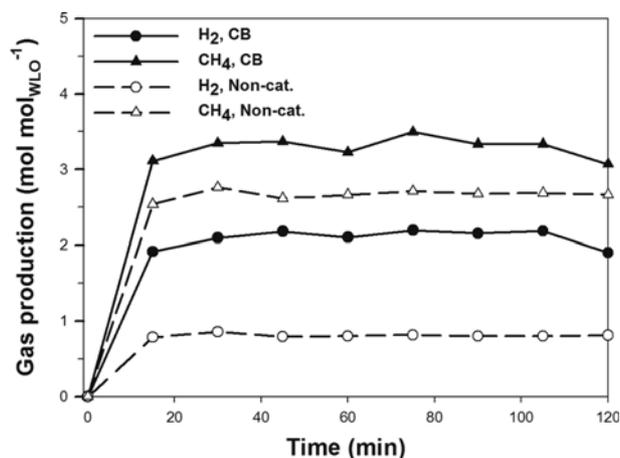


Fig. 5. Comparison of gas production under non-catalytic and carbon black at 750 °C.

greater than that without carbon catalyst. Therefore, we may conclude that the carbon black catalyst was effective in the production of methane from WLO and in the production of hydrogen from methane, and ethylene. The difference in the production rate of hydrogen with and without the carbon black catalyst was also greater than that of methane. From this experimental result, it can be determined that the carbon black catalyst provided better catalytic activity in the hydrogen production from methane and ethylene such as  $\text{CH}_4 \rightarrow \text{C} + \text{H}_2$  and  $\text{C}_2\text{H}_4 \rightarrow 2\text{C} + 2\text{H}_2$  rather than methane production from propane such as  $\text{C}_3\text{H}_6 \rightarrow \text{CH}_4 + 2\text{C} + \text{H}_2$  and  $\text{C}_3\text{H}_6 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_4$ , and from butane  $\text{C}_4\text{H}_{10} \rightarrow \text{CH}_4 + \text{C}_3\text{H}_6$ .

The TEM images of fresh carbon black and used carbon black under reaction conditions of 800 °C and 2 hrs after the decomposition of WLO are given in Fig. 6(a), and (b) respectively. As shown in Fig. 6(a), a smooth round image of the surface of fresh carbon black was observed. However, in Fig. 6(b) there are several protrusions on the specific location of the carbon black. Therefore, it is believed that the sharp edge protrusion at specific locations pro-

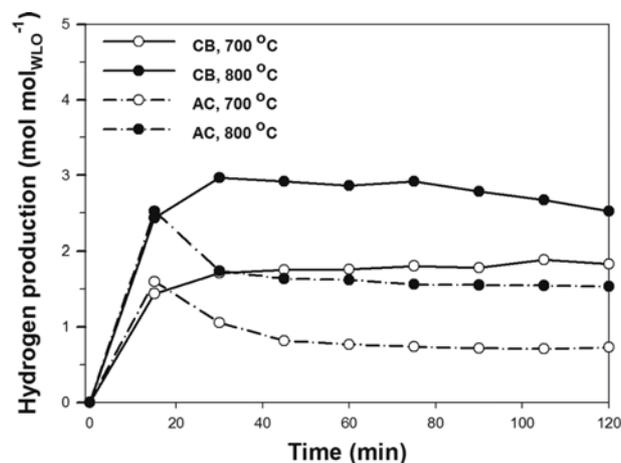


Fig. 7. Effect of temperature on hydrogen production over carbon catalysts at 700 °C and 800 °C.

vided the active sites for hydrogen and carbon production from methane and ethylene. Since the size of the protrusion increases as the reaction proceeds, the deposited carbon of the reaction product grew on that spot and provided a new active site for the next reaction. Four protrusions were observed in the lower part of Fig. 6(b) and this TEM image also supported the catalytic activity of carbon black in the production of hydrogen and carbon from methane and ethylene.

### 3. Temperature Effect on Hydrogen Production with and Without Catalyst

It was expected that the higher reaction temperature resulted in the faster decomposition of WLO, and thus increased the production of shorter hydrocarbons such as methane, ethylene and ethane. Therefore, a larger hydrogen production rate was expected. The effect of temperature on the hydrogen production rate on activated carbon and the carbon black catalyst is provided in Fig. 7. Notice that the increase in temperature increased the reaction rate, and a greater gas production rate of hydrogen was obtained.

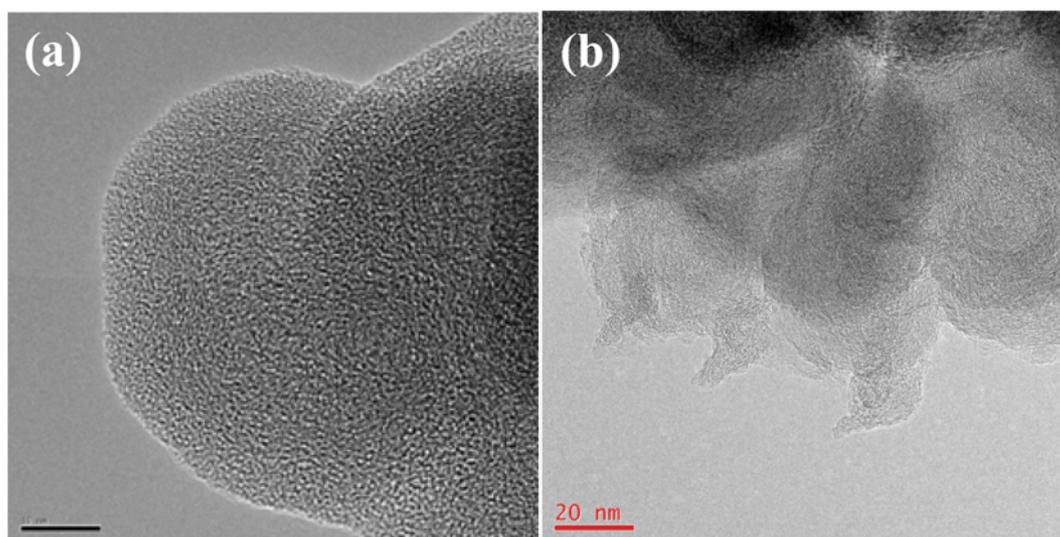


Fig. 6. TEM image of (a) fresh carbon black (N330) and (b) used carbon black at 850 °C.

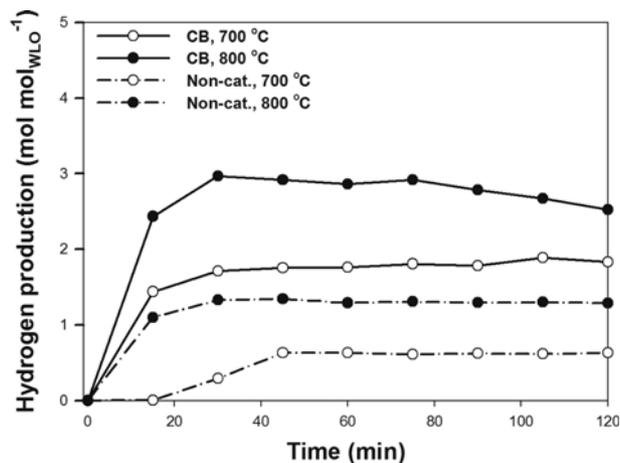


Fig. 8. Effect of temperature on hydrogen production under non-catalytic and carbon black at 700 °C and 800 °C.

Also, as seen in the previous section, carbon black catalyst showed higher catalytic activity in the production of hydrogen than that of activated carbon, and activated carbon showed deactivation due to carbon coking during the hydrogen production from the WLO. The effect of temperature on the hydrogen production under non-catalytic and carbon black catalyst is given in Fig. 8. As can be seen, the hydrogen production rate increased from 0.6 mol to 1.7 mol under non-catalytic conditions and from 1.3 mol to 2.8 mol with the carbon black catalyst. This implies that the increase of temperature from 700 °C to 800 °C resulted in a 200% increase in hydrogen production. Therefore, we conclude that the production of hydrogen from the decomposition of WLO favored higher temperatures, and the thermo-catalytic decomposition of WLO was more strongly dependent on the reaction temperature than the thermal only decomposition reaction.

#### 4. Product Distribution and Gas Composition from the Decomposition of WLO

The product distribution from the decomposition of WLO and gas composition of product gas was analyzed. Fig. 9 shows the yield of hydrogen, methane, ethylene and carbon from the non-catalytic

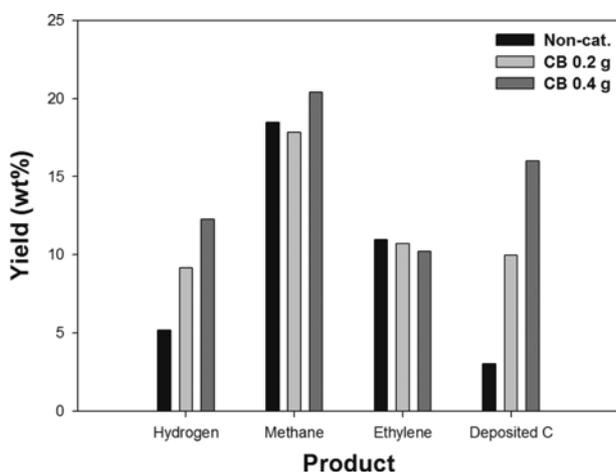


Fig. 9. Effect of catalyst loading on product distribution.

Table 4. Mole composition of hydrogen and methane at 800 °C

(% mole)	H <sub>2</sub>	CH <sub>4</sub>
Non-catalytic	18.69	45.96
Activated carbon	22.06	47.16
Carbon black	41.06	44.59

and catalytic decomposition of WLO. Here, the carbon black catalyst produced more hydrogen and carbon than non-catalytic condition, and the production yield of methane and ethylene was almost the same value for catalytic and non-catalytic decomposition of WLO. The higher production yield of deposited carbon with the carbon black catalyst also demonstrated that carbon black was effective in the production of hydrogen and carbon from methane and ethylene. In previous research concerning the production of hydrogen from waste mineral oil by thermocatalytic decomposition [12], a composition of 63 wt% of solid, 35 wt% of gas, and 2 wt% of liquid fuel was obtained with Ni catalyst at a temperature of 700 °C. In this work with carbon black catalyst, 11 wt% of solid, 81 wt% of gas product and 8 wt% of liquid were obtained at a temperature of 800 °C as shown in Table 3. The higher gas portion of product distribution in this work probably resulted from the higher operating temperature. Thus, the product distribution of waste lubricating oil was strongly dependent on the origin of lubricating oil and operating temperature. Lazaro et al. [12] employed automobile lubricating oil, and we used aluminum rolling lubricating oil in this study. Furthermore, the composition of gas product of this study was also compared with gas composition from the result of Lazaro et al. [12]. In this work with carbon black catalyst, hydrogen was 41 mol% and methane was 45 mol%, and with activated carbon catalyst, hydrogen was 22 mol% and 47 mol% of methane were obtained at 800 °C as shown in Table 4. In comparison, Lazaro et al. [12] reported that hydrogen of 64 mol% and methane of 31 mol% were obtained with activated carbon at 850 °C. Hence, we can conclude that the process of thermo-catalytic decomposition of waste lubricating oils produced both hydrogen and methane as the major gas products.

## CONCLUSIONS

The thermo-catalytic decomposition of waste lubricating oils for the production of hydrogen and methane over carbon catalysts was investigated. The major decomposition products of lubricating oils over carbon catalysts were hydrogen, methane, ethylene in a gas phase, carbon in a solid phase, and tar in a liquid phase. Activated carbon and carbon black showed catalytic activity in the production of hydrogen and methane from the decomposition of waste lubricating oils. Under the same reaction conditions, carbon black displayed greater hydrogen and methane production rates and lower ethylene production rates than activated carbon. The temperature effect on the gas production was significant over carbon black catalyst and two-times higher hydrogen production rate was obtained as the temperature increased from 700 °C to 800 °C. The product distribution from the thermo-catalytic decomposition of WLO over the carbon black catalyst at the temperature of

800 °C was 11 wt% of solid, 81 wt% of gas and 8 wt% of liquid, and the product gas composition was 41 mol% of hydrogen and 47 mol% of methane. The carbon black catalyst was found to be an effective catalyst in the production of hydrogen and methane from the thermo-catalytic decomposition of waste lubricating oils.

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