

Research Article

Characterization and Application of Aluminum Dross as Catalyst in Pyrolysis of Waste Cooking Oil

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Abstract

Aluminium dross, a waste material produced by dissolution of aluminum scrap, was characterized physically and chemically by various analysis techniques for a potential to be used as catalyst. Using catalyst from waste materials reduced the cost for synthesizing of new catalyst. An efficient catalyst derived from industrial solid waste was modified by acid washing for using in a pyrolysis of waste cooking oil. The modification of aluminum dross resulted in increased surface area (from 0.96 to 68.24 m²/g), acidity (from 315 to 748 μmol/g) and thermal stability. Pyrolysis waste cooking oil was used to test the performance of aluminum dross as catalyst before and after modification. The product analysis showed a better result than the unmodified material based on increased yield of bio-oil and improved selectivity. Copyright © 2017 BCREC GROUP. All rights reserved

Keywords: Al dross; Thermal activation; Chemical activation; Pyrolysis waste cooking oil

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1. Introduction

Recently, the researchers have applied catalytic materials which derived from waste materials. In some processes, using catalyst can pose largest monetary cost so that the efforts forward to search catalyst from waste materials. In addition, sustainability has become a sign and significant factor in modern society. Waste materials not only grant alternative renewable source, but also provide a resource to synthesize catalysts [1].

Aluminum dross is by-product that is formed after aluminum liquefied in a customary purging or reusing procedures. Around 5 million tons of aluminum dross is generated every year around the world [2]. Substantial amounts of the dross are discarded in landfills poisoning health, natural and security peril issues in light of its poisonous quality and high combustibility. On the other hand, recycling 1 kg of aluminum waste save about 4 kg of bauxite, 2 kg of chemicals, and 7.5 kWh of electricity [3]. Aluminum (Al) dross can be classified as three types namely white, black and salt cake, depending on the amount of aluminum present and the morphology of the wastes [4]. The main components of the dross are metallic alumi-

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num, aluminum oxides, aluminum chlorides and oxide of transition metals [2]. Therefore, Al dross considers as valuable material and there is much legitimacy if the dross that is shaped could be "reused" as an engineering item for particular applications.

Various studies have reported on the application of dross as an alternative material of Al for the preparation of catalytically active materials. Balakrishnan *et al.* [5] reported that zeotype $\text{AlPO}_4\text{-}5$ was synthesized by the reaction of dross with phosphoric acid. Kim *et al.* [6] prepared $\text{CrAPO}\text{-}5$ (the chromium-containing analogue of $\text{AlPO}_4\text{-}5$) by using Al dross and identical properties were obtained with sample prepared by $\text{Al}(\text{OH})_3$. Das *et al.* [7] produced η -alumina from waste Al dross by leaching, hydrolyzing and calcination. In short, Al dross can be utilized as an alternative material of Al for preparation of the catalysts.

Pyrolysis is an effective and easy method for bio-fuel production. Kerosene, gasoline and diesel can be produced from catalytic pyrolysis in faster manner [8]. Using industrial waste as catalyst and utilize it to enhance the pyrolysis process can be considered as promising technologies in reducing the amount of waste generated from human activities and industrial processes. Bauxite which considers a rock consisting essentially of one or more aluminum hydroxide minerals has been tested as catalyst for catalytic cracking of soybean oil. The product generated showed better results than thermal cracking due to low quantity of acid present in the bio-oil. The presence of catalyst increase decarboxylation reaction of the carboxylic acids formed in primary cracking [9]. Red mud was used in pyrolysis of hemp-seed to produce bio-oil. The red mud was used after going through reduction process by acetic acid and formic acid. The reduced red mud upgraded bio-oil because the product consists of fewer carbonyl-containing and polar oxygenated compounds with more saturated hydrocarbon [10]. Blast furnace slag (BFS) was used in pyrolysis of waste sunflower oil. The product was rich with paraffinic content and lower naphthenic content [11].

Based on reported literatures, Al dross which is a waste material producing from aluminum processing still have value added materials that can be either recovered or treated using various techniques and have a potential to be used as catalyst. Instead of just disposed of, Al dross will be used as a raw material for this study. Detailed characterization of the Al dross will be performed. Modification of the Al dross for potential use as catalyst will also be con-

ducted, and finally utilization of the Al dross in a pyrolysis of waste cooking oil for catalytic performance evaluation before and after modification process will be executed.

2. Material and Method

2.1. Materials

Al dross used in this study was supplied from Malaysian recycling company. Hydrochloric acid (HCl) with 37% purity was obtained from R&M Company. Waste cooking oil, which generated after frying vegetables, chicken, and meat, collected from residential area, was used for pyrolysis reaction. The oil was centrifuged at 6000 rpm for 30 min and was then filtered to remove food residue. The oil obtained from centrifuging was used directly without further purification.

2.2. Procedure

For catalyst preparation, the sample was sieved to remove coarse and foreign particles and then ground by ball mill grinder for 1.5h. After that, the sieved ground sample was passed through a 300 μm sieve. The method used to activate the sample of Al dross includes the followings: firstly; calcination in tubular furnace at 700 °C with heating rate 10 °C/min for 5 hours. For acid washing treatment, 5 g sample was immersed into the solution prepared from 20 mL HCl with 80 mL H_2O with continuous stirring conditions at room temperature for 3 h. The acid washed sample was then filtered and washed with deionized water until the pH value of the washing water was neutral. The sample was dried by an oven (Mettler, model EU-200) at 100 °C for 24 h and then subjected to the calcination process by using tubular furnace at 600 °C for 3 h at heating rate of 10 °C/min.

The pyrolysis of waste cooking oil was performed to test the activity of material as catalyst. Pyrolysis reactions were carried out in a fractionated cracking system as shown in Figure 1. The round flask waste was heated using stirring mantle (Misung Scientific Co. Ltd., model MS300). The reaction temperatures of 390-420 °C were chosen for batch cracking. The round flask was loaded with 150 g of waste of cooking oil. Then 5% catalyst was added to the oil. The mixture in the flask was then purged with nitrogen for oxygen free environment and heated to reaction temperature with heating rate at 20 °C/min. The liquid products were collected in a glass trap (receiving flask). The run period was kept 30 min. At the end of experi-

ments, the respective amount of the liquid and residual oil-coke were measured. The yield was calculated from Equation (1) and selectivity of carbon number was determined by comparing the peak area of obtained spectra with the peak area of the standard using Equation (2) [12, 13]. In order to confirm the reproducibility of the results, the experiments were conducted for three times.

$$\text{Yield}(\%) = \frac{\text{pyrolysis oil product}}{\text{feed}} \times 100\% \quad (1)$$

$$\text{Selectivity}(\%) = \frac{\text{Area of the desired product}}{\text{Total area of the product}} \times 100\% \quad (2)$$

2.3. Characterization of catalyst

To examine the changes that happen to Al dross, the unmodified and modified material were characterized using various characterization techniques. Chemical composition of the unmodified and modified material was conducted using X-ray fluorescence spectroscopy (model Philips PWI 404). The specific surface area and pore volume were measured by Brun-

auer-Emmett-Teller (BET) apparatus (Quantachrome, model Atosorb-1, USA). The thermogravimetric study was performed by using a thermogravimetric analyzer (model Mettler Toledo, TGA/SDT851, USA). The morphology of the material was investigated using SEM instrument (HITACHI, S-3400N, JAPAN). Temperature programmed desorption using NH_3 (TPD- NH_3) was utilized to measure the acidity of the catalyst (Thermo Finnigan, model TPDRO 1100 series).

2.4. Characterization of bio-oil

The functional groups of bio-oil was determined by Fourier Transform Infrared Absorption (FTIR) spectra instrument (model Perkin-Elmer 100 series, USA). In addition, the bio-oil products were quantitatively identified using alkane standards ($\text{C}_7\text{-C}_{20}$), obtained from Sigma Aldrich. The analyses of cracking products were quantified using gas chromatography (Shimadzu GC-1413). The column used was a HP-5 capillary column (32 m \times 0.25 mm and 0.25 thicknesses) with flame ionization detector (FID) operating at 300 $^\circ\text{C}$. The bio-oil product was diluted with GC grade n-hexane before injection for the yield analysis. The injector temperature was 300 $^\circ\text{C}$, and the injector split ratio was set to 10:1. The flow rate of the N_2 carrier gas was 1 mL/min. The oven temperature was programmed to hold at 50 $^\circ\text{C}$ for 6 min, then ramp at 7 $^\circ\text{C}/\text{min}$ to 270 $^\circ\text{C}$ and hold at that. All bio-oil samples produced from the pyrolysis were tested for catalyst performance in terms of bio-oil yield and selectivity.

3. Results and Discussion

3.1. Characterization of the catalyst

X-ray fluorescence spectroscopy showed Al dross as a complex oxidic material, was formed when molten aluminum comes in contact with air at the outer surface of the melt. The main constituents of the raw material include Al_2O_3 , Cl , Fe_2O_3 , and K_2O , with almost equal amounts of CaO , CuO , and SiO_2 and small amounts of other metal oxides as shown in Table 1. The chemical and mineralogical composition of Al dross depends mainly on the quality of Al scrap processing, the operating conditions, and the type of technology and furnace applied for Al metal production [14]. The acid washing characterization showed the increasing Al_2O_3 content after HCl washing. This effect could be explained by two reasons as follows. First, prior to acid washing, the raw material was subjected to grinding using a ball mill and subse-

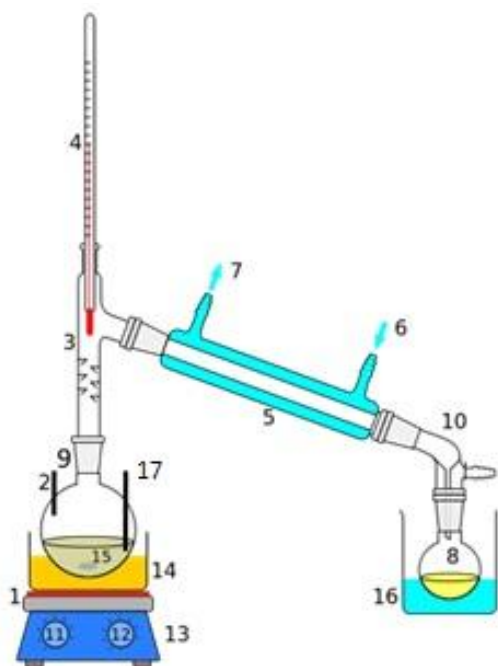


Figure 1. System used in the cracking process: 1: A heating device 2: Nitrogen gas inlet 3: Still head 4: Thermometer 5: Condenser 6: Cooling water in 7: Cooling water out 8: Distillate/receiving flask 9: Still pot 10: Still receiver 11: Heat control 12: Stirrer speed control 13: Stirrer/heat plate 14: Heating (sand) bath 15: mechanical stirrer 16: Cooling bath 17: Thermocouple.

quent sieving with a <300 μm mesh. According to Hwang *et al.* [15] and Tsakiridis *et al.* [14], metallic aluminum could be recovered by screening and sieving after crushing and grinding the original Al dross. Second, Das *et al.* [7] reported that when Al dross was subjected to acid treatment with 15% H₂SO₄ concentration, the material recovered alumina at around 71% yield. Therefore, alumina content increased to 593.59 mg.g⁻¹, when the Al dross was treated with acid at 20 wt%. The chloride content disappeared from the Al dross after conducting a treatment by Miskufova *et al.* [16] in which HCl was adopted to leach out all chloride content. This method was first employed when the groups studied Al leachability from aluminum dross fines after mechanical pretreatment in alkaline solution at atmospheric conditions.

Table 1. Component analysis of the Al dross

Metal oxides	Composition analysis (mg.g ⁻¹)	
	Raw material	Acid washing
Al ₂ O ₃	390.97	593.59
Cl	222.83	n.d.
Fe ₂ O ₃	124.05	149.31
K ₂ O	96.24	17.16
CaO	35.71	18.72
CuO	33.83	58.31
SiO ₂	30.07	73.13
ZnO	16.01	19.67
MnO	13.15	14.52
TiO ₂	9.69	11.97
BaO	8.70	16.78
SO ₃	5.62	11.03
Cr ₂ O ₃	4.94	6.57
SrO	3.22	2.21
NiO	2.68	4.33
Br	0.87	n.d.
Ac	0.79	1.4

Note: n.d. = not detected

Table 2 shows the surface area analysis in the raw Al dross (unmodified) and modified material. After acid washing, it was observed a sharp increase in BET surface area and pore volume to 68.24 m²/g and 0.34 cm³/g, respectively. This increase could be due to dissolution of oxidizing deposits which were initially blocking the pore opening. According to the International Union of Pure and Applied Chemistry (IUPAC), Figure 2a shows the adsorption-desorption of N₂ displaying type of isotherm III, indicating the presence of macroporous (>50 nm) structures. The majority of these structures comprise macroporous regions with low surface areas as shown in Table 2, which means the interaction was very weak with the adsorbent molecules. The isotherm suggests a multilayer adsorption process. The hysteresis loop type H3 reveals a macroporous structure for flaky plate particles; this result is in agreement with the SEM analysis (Figure 3a). On the other hand, the Al dross material after con-

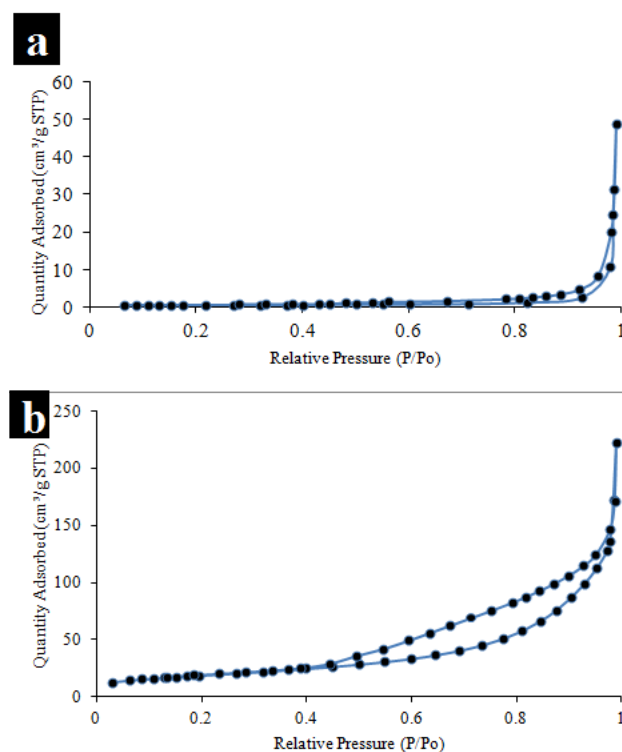


Figure 2. Isotherm of Al dross (a) raw material and (b) modified material.

Table 2. Pore characteristics of the Al dross

Al dross	Raw material	Acid washing method
BET surface area (m ² /g)	0.96	68.24
Pore volume (cm ³ /g)	0.06	0.34
Average pore diameter (nm)	283.28	20.24

ducting acid washing with HCl shows isotherm V with hysteresis loop type H1, indicating an increase mesopore structure through its hysteresis loop, that is, the non-overlapping portion of the adsorption and desorption branches. The SEM image as shown in Figure 3b displays the changes after modification.

Thermogravimetric study was performed to verify the thermal stability of the material. Thermal stability refers to the ability of a substance to resist property changes under heat. The raw material (unmodified) did not show thermal stability (Figure 4a) upon testing. The weight curve sharply plummeted by around 0.7%; such weight loss could be attributed to the loss of water molecules caused by crystallization. However, following the decrease in weight, a subsequent weight increase occurs after the temperature exceeded 520 °C. This increase in weight is likely due to oxidation. By contrast, the acid washing method affords the Al dross good thermal stability as shown in Figure 4b because the process triggered the molecules to exhibit higher resistance against decomposition at high temperatures.

The catalyst surface concentrations of acidic centers was measured by temperature programmed desorption of ammonia (TPD-NH₃). The TPD spectra of the adsorbed ammonia on the unmodified Al dross as portrayed in Figure 5a indicate the presence of medium acid sites

with a density of 315 μmol/g at 520 °C. By contrast, after acid washing of the Al dross with HCl and calcination for 3 h at 600 °C, the TPD spectra of the adsorbed ammonia (Figure 5b) show two peaks. The first peak is noted at temperature 321 °C belongs to weak acid site. Whereas, the second peak at temperature 909 °C exhibits stronger acid site. The total amount of gas adsorbed by the sample is 748 μmol/g. The increased acidity of the modified material was due to the enlargement in the surface area and pore volume.

3.2. Characterization of bio-oil

3.2.1. Functional group analysis of bio-oil

To measure the catalytic performance of the catalyst, both acid-treated and unmodified Al dross were applied in the pyrolysis of waste cooking oil together. The results were compared with non-catalytic pyrolysis of waste cooking oil as thermal cracking. FT-IR analysis was performed to examine the chemical functional groups present in the bio-oil produced from the pyrolysis. An important observation on the bio-oil is that the composition of the pyrolysis oil resembled that in the original biomass (waste cooking oil) but was drastically different from those in petroleum-derived fuels

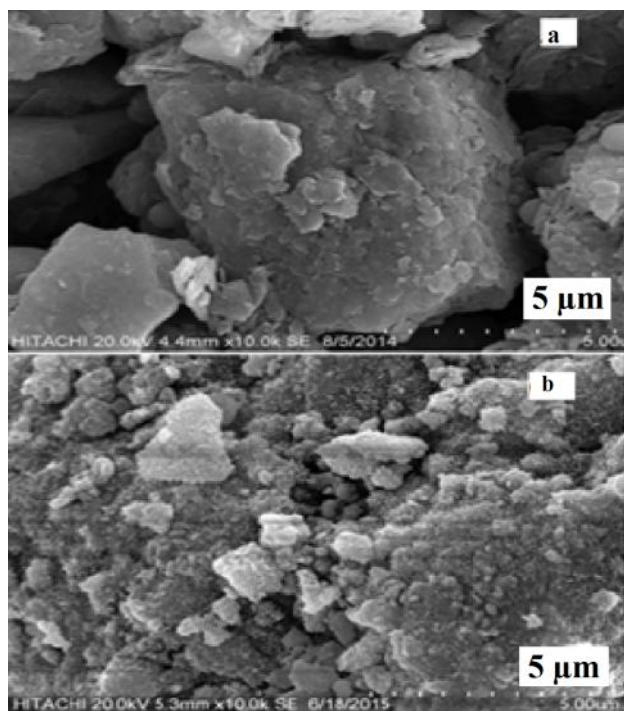


Figure 3. SEM morphology of Al dross (a) raw material and (b) modified material.

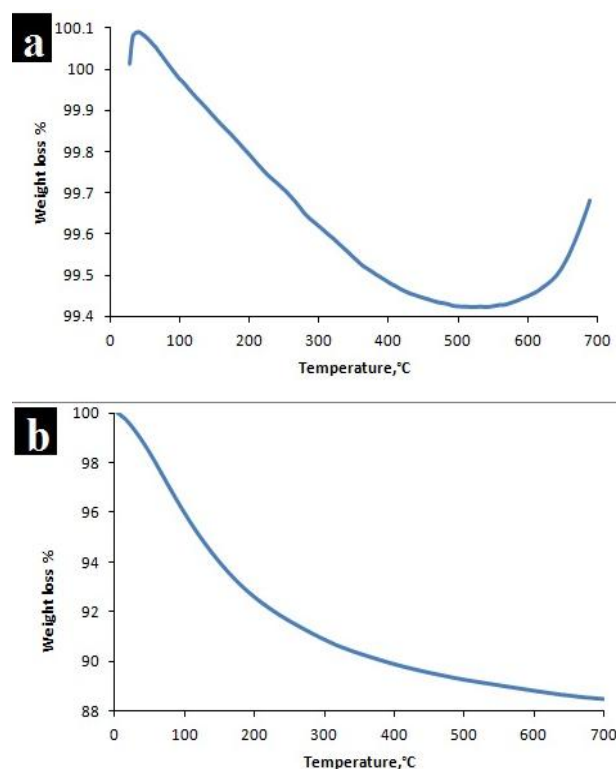


Figure 4. TGA of Al dross for (a) raw material and (b) modified material.

[17]. Figure 6 displays the comparison of main functional groups between waste cooking oil and bio-oil produced using Al dross before and after modification. The pyrolysis oil (bio-oil) shows characteristic vibrational modes at 2850-3000 cm^{-1} for the C-H stretching in alkanes, 1000-1320 cm^{-1} for the C-O stretching in carboxylic acid, 910-950 cm^{-1} for the O-H bending in carboxylic acid, and 720-725 cm^{-1} for the C-H rocking in alkanes [18,19].

An extremely broad absorption peak centering at 1185 cm^{-1} for the C=O stretching in carboxylic acid is observed in the spectra of the waste cooking oil. This peak could be a measure for the progress of deoxygenation cracking reactions. This peak does not present in the cracking products under untreated and treated Al dross catalyst. The appearance of new peaks

of C-O stretching at 1285 cm^{-1} and O-H bending at 910 cm^{-1} in the bio-oil indicates the presence of carboxylic acid in small amounts. In addition, a slight shift in FT-IR peak (1710 cm^{-1}) in the deoxygenated product denotes the C=O of the carboxylic acid group, which is consistent with the findings of Asikin-Mijan *et al.* [20]. The lower intensity of this band at 1710 cm^{-1} could be credited to the amount of carboxylic acid decreased after the pyrolysis. The spectrum of functional group based on IR adsorption is tabulated in Table 3.

3.2.2. Chromatographic analysis of the bio-oil

The yield of bio-oil produced from catalytic pyrolysis of waste cooking oil showed the increment when using with untreated and modified catalysts compared to thermal cracking as shown in Figure 7. The increase of bio-oil yield could be attributed to metal oxide contained in these materials as shown in the XRF characterization of the waste materials before and after treatment (Table 1). This proves that the catalytic properties of metal oxides become ap-

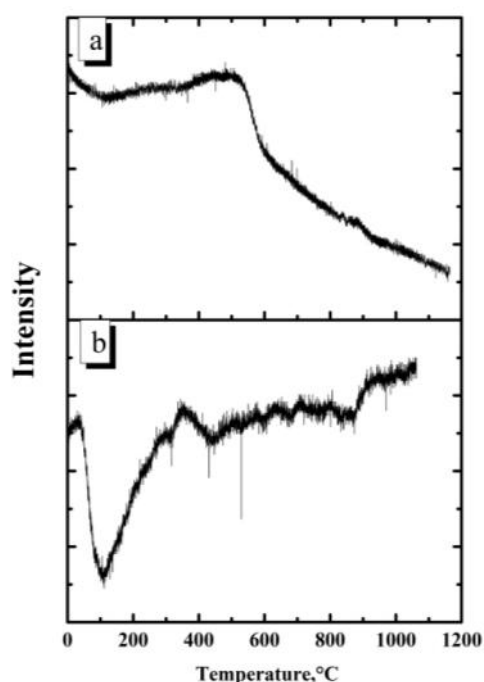


Figure 5. TPD-NH₃ analysis for Al dross (a) raw material and (b) modified material

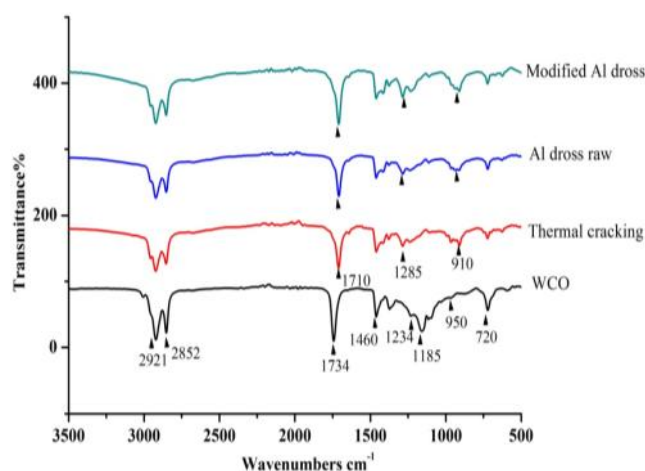


Figure 6. FT-IR spectra of bio-oil produced

Table 3. Summary of characteristic IR absorption for bio-oil.

Functional groups	Vibration modes range (cm^{-1})	Bio-oil characteristic absorption peaks (cm^{-1})
C-H stretch	2800-3000	2852, 2921
C=O stretch	1600-1750	1710, 1743
C-H bend	1350-1470	1372, 1460
C-O stretch	1000-1320	1185, 1234, 1285
O-H bend	910-950	910, 950
C-H rock	720-725	721, 722, 723

parent from the adsorption of reactants on the unsaturated metal sites and/or oxygen atom, followed by addition or elimination of hydrogen and/or oxygen [8]. The bio-oil yield produced from catalytic cracking by untreated and treated Al dross was 14 and 16%, respectively. The slight increase in the bio-oil yield could be ascribed to higher BET surface area (Table 2) and acidity to 748 $\mu\text{mol/g}$ of treated Al dross. In addition, the increase in the amount of aluminum oxide (Al_2O_3) contained in Al dross after acid washing as shown in XRF (Table 1) might contribute to the slight increment of the bio-oil yield. Some studies on pyrolysis of canola oil and sunflower oil using aluminum oxide as catalyst proved the increment in the bio-oil yield [21,22].

For obtaining a detailed understanding of the selectivity of each catalyst toward n-alkane and n-alkene obtained from the catalytic pyrolysis, the composition was analyzed by GC analysis. Figure 8 shows the bio-oil compounds grouped according to their carbon number. It can be seen the bio-oil produced at 390-420 $^\circ\text{C}$, are a mixture of C_7 - C_{20} . The figure shows significant change between pyrolysis with raw material (untreated) and modified (treated) Al dross in the selectivity to carbon number. Pyrolysis with untreated Al dross shows sharp peak at C_7 , whereas acid-treated Al dross selected to C_9 and C_{15} . Even though only slight increment of bio-oil yield was obtained from the pyrolysis of waste cooking oil using untreated and treated Al dross, different selectivity of the product was observed. This difference might correlate to increase BET surface area and acidity.

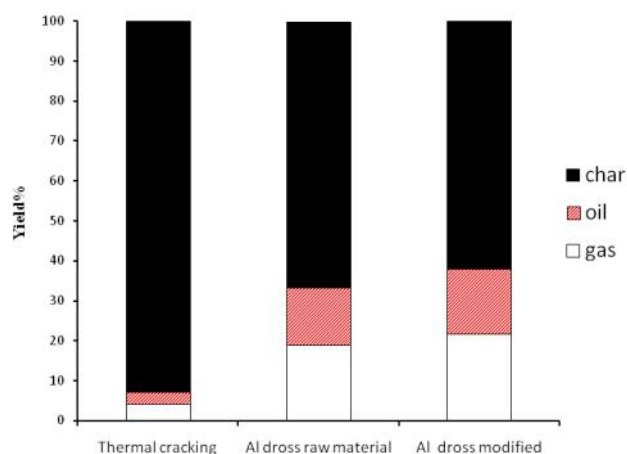


Figure 7. Yield percentage of bio-oil from catalytic pyrolysis

4. Conclusions

The characterization of Malaysian Al dross reveals that this an inexpensive waste material contains precious amount of metal oxides which exhibit cheap source as catalyst. However, several characterization analyses such as surface area, morphology of the surface, thermal stability and acidity showed poor properties of the Al dross. A simple chemical activation by acid washing method changed most properties of the material. An increase in surface area and acidity enabled Al dross as potential catalyst candidate in catalytic reactions. The performance of the material in pyrolysis of waste cooking oil proved modified Al dross represent as a good candidate in the cracking reaction.

Acknowledgement

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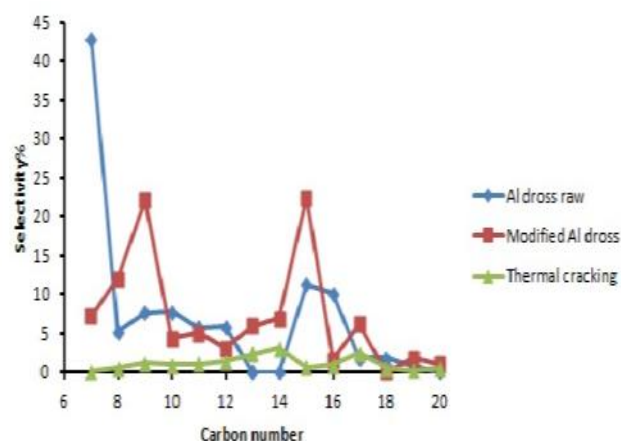


Figure 8. Selectivity of carbon number for Al dross

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