Research Article

Characterization and Application of Molten Slag as Catalyst in Pyrolysis of Waste Cooking Oil

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Abstract

Chemical and physical analysis was performed to identify the molten slag composition and its ability to be used as alternative catalyst in pyrolysis of waste cooking oil. The implementation such type of catalytic material could be useful in reducing the process cost. To increase the efficiency (increase the active site) of molten slag, it was modified by acid washing that resulted in an increase in the acidity from 159 to 1224 µmol/g. The results showed that the yield of bio-fuel was increased and the product selective to n-C_{15} upon the modification of molten slag by acid treatment. Copyright © 2020 BCREC Group. All rights reserved

Keywords: Molten slag; Thermal activation; Chemical activation; Pyrolysis; Bio-fuel

1. Introduction

Recently, industrial solid waste attracts scientists since sustainability has become a sign and guiding principle for modern society. Waste material can offer a worthy source of energy, construction materials, chemicals and high value functional products such as catalyst [1].

Slag is generated from iron and steel making as byproduct. Different types of steel slag, each named for the process from which they are generated, include blast furnace slag (BFS), basic oxygen furnace slag (BOF), electric arc furnace acid slag (EAF), and ladle furnace basic slag (LF). The first type is also called iron-making slag, whereas the latter three are also called converter/refining slag [2]. Slag contains a quantity of valuable metals and is considered as a secondary resource of metals rather than an end-waste. Slag has been applied as a source of materials in numerous areas such as construction material, adsorbent and catalyst [3,4].

The use of molten slag as an alternative source of catalyst has been reported because of low cost and high volume of by-product by many researchers. Kuwahara and colleagues synthesized a hydrotalcite-like compound from BFS via acid leaching with HCl followed by precipitation. The product was identified as Ca-based hydrocalumite. The performance of Ca–Al-based hydrocalumite was tested in many chemical reactions such as transesterification of soybean oil, cycloaddition reaction of epoxides and Knoevenagel condensation. The researchers proved the synthesized catalyst gave good yield

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in all reactions [2,5,6]. Bermudez *et al.* utilized steel-making slag as a catalyst for microwave-assisted dry reforming of CH_4. Conversion achieved by using this molten slag after was 80% [7]. Wang *et al.* prepared a catalyst from waste slag by dissolution with HCl and co-precipitation with NaOH and tested in diethyl carbonate synthesis via ethanolysis of ethyl carbamate and the yield of diethyl carbonate was 33% [8]. Kar & Gurbuz used blast furnace slag as received in pyrolysis frying sunflower oil. The yield of organic liquid product was 82.5% and it possessed the important hydrocarbon compounds in the range of C_8-C_{14} atoms [9].

Catalyst performance was investigated by pyrolysis. Pyrolysis is a thermo-chemical process in which organic materials are converted into a carbon-rich solid and volatile (liquid and gases) product in the absence of oxygen [10]. 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 [10-12]. To achieve high conversion in liquid fuels, the bio-oil quality in catalytic upgrading is strongly dependent on the properties of the catalyst, including structure, acidity, and pore size, as well as the type of feedstock and reaction conditions. Among these factors, catalyst acidity performs the most critical function in upgrading reactions, including cracking, oligomerization, deoxygenation, alkylation, aromatization, cyclization, isomerization, and polymerization [13].

Based on cited works, the byproduct of iron and steel making industry is enriched with different types of minerals that could be used as a catalyst for different reactions. The present work focuses on characterization of the Malaysian molten slag and the possibility of its application in pyrolysis of waste cooking oil after simple treatment. Therefore, project is aimed to study waste material; molten slag and modified molten slag (using acid washing technique) as potential and alternative catalyst in converting WCO to biofuel via catalytic pyrolysis process.

## 2. Materials and Method

2.1 Materials

Molten slag was purchased from Malaysian recycling company. Hydrochloric acid (HCl) used in this study with 37% purity was supplied from R&M Company. The waste cooking oil was collected from residential area and used after simple treatment as shown in the procedure section.

2.2 Procedure

To remove the unwanted material from the waste oil, the waste oil was subjected to centrifuge at 6000 rpm for 30 min. After that the oil was filtered (to remove food residue) and used directly without further purification.

The sample was sieved to remove the impurities such as coarse and foreign particles. After that, it was ground by ball mill grinder for 1.5 h following by sieving through a 300 µm mesh. To increase the active site of the catalytic material (molten slag), it was treated with diluted acid. 5 g of molten slag was immersed into diluted HCl solution (1:4) with continuous stirring at ambient temperature for 3 h. Then, the mixture was filtered and washed with deionized water to remove the acid traces and reached to 7 of pH value. The prepared sample was then dried by an oven (Memmert, model EU-200) at 100 ºC for 24 h and then aimed to the calcination process using tubular furnace at 600 ºC for 3 h at interval of 10 ºC/min.

The pyrolysis reaction using waste cooking oil was achieved to investigate the prepared catalyst activity. The pyrolysis reactions were performed in a fractionated cracking system as indicated in Figure 1. In which, the waste oil was heated using stirring mantle (Misung Scientific Co. LTD, model MS300) at reaction temperatures of 390-420 ºC. The reaction flask was provided with 150 g of waste of cooking oil and then 5% of catalyst was added to the reaction flask. For oxygen free environment, the mixture in the flask then purged with nitrogen gas and the heating rate was increased by 20
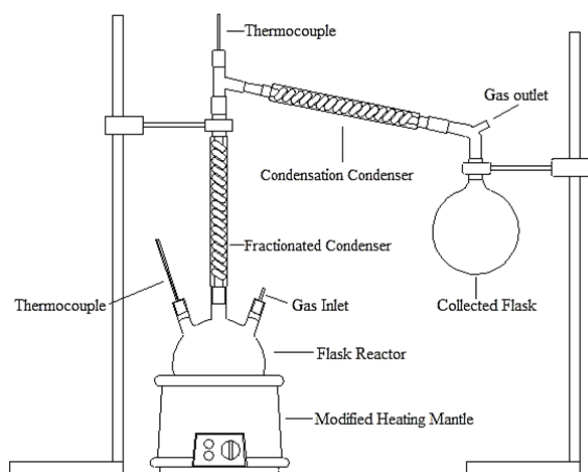
Figure 1. Fractionated cracking system used in the cracking process.

ºC/min. The reaction products were collected in a glass trap along the experiment run (30 min). When the reaction time reached to the end, both of the produced liquid and residual oil-coke were measured using digital balance. To maintain the accuracy and reproducibility of the reaction, all the experiments were performed three times and their average was recorded. The reaction yield and selectivity were calculate using Eq. 1 and Eq. 2, respectively [14,15]:

$$Y = \frac{P}{F} \times 100\% \quad (1)$$

$$S = \frac{C_x}{\sum n_x} \times 100\% \quad (2)$$

where P is pyrolysis oil product, and F is feed of WCO, C_x is area desired hydrocarbon fraction and n_x is area of hydrocarbons.

2.3 Characterization of Catalyst

To examine the changes that happen to molten slag, the unmodified and modified material were characterized using various characterization techniques. Chemical composition of the unmodified and modified material were conducted using X-ray fluorescence spectroscopy (model Philips PWI 404). The specific surface area and pore volume were measured by Brunauer-Emmett-Teller (BET) apparatus (Quantachrome, model Atosorb-1, USA). The morphology of the material was investigated using SEM instrument (HITACHI, S-3400N, JAPAN). Temperature programmed desorption using NH₃ (TPD-NH₃) was utilized to measure the acidity of the catalyst (Thermo Finnigan, model TPDRO 1100 series).

Table 1. Component analysis of molten slag.

Metal oxides (%)	Raw material	Acid wash method
Fe_2O_3	53.81	94.66
CaO	31.13	0.91
ZnO	6.08	0.49
SiO_2	5.16	n.d.
MnO	1.27	2.52
SO_3	1.38	0.27
K_2O	0.32	n.d.
Cr_2O_3	0.28	1.05
CuO	0.20	0.11
Ac	0.19	n.d.
PbO	0.09	n.d.
SrO	0.05	n.d.
NiO	0.04	n.d.

2.4 Characterization of Bio-fuel

Fourier Transform Infrared (FTIR) technique (Perkin-Elmer 100 series, USA) was used to identify the functional groups of bio-fuel. The identification of bio-fuel products and its quantity were performed using alkane standards (C_7-C_{20}) which obtained from Sigma Aldrich. The pyrolysis products were quantified using gas chromatography (GC) (Shimadzu GC-1413) using capillary column type HP-5 (32 m × 0.25 mm and 0.25 thicknesses) with flame ionization detector (FID) that operating at 300 ºC. Before sample injection and for yield analysis, the bio-fuel sample was diluted with GC grade n-hexane. The injector temperature was maintained to 300 ºC, while the injector split ratio was set to 10:1. The flow rate of the nitrogen carrier gas was set to 1 ml/min. The oven temperature was set in three stages: hold at 50 ºC for 6 min, ramp at 7 ºC/min to 270 ºC and hold at the final temperature (270 ºC). It is important to mention here that catalyst performance was evaluated using yield and selectivity of bio-fuel samples that produced from the pyrolysis reactions.

3. Result and Discussion

3.1 Characterization of the Catalyst

In order to utilize molten slag as catalyst, components analysis by XRF for as received and treated materials were conducted as shown in Table 1. The main constituents compounds are Fe_2O_3, CaO, ZnO, and SiO_2 with low contents of ZnO, SiO_2, MnO, K_2O, SO_3, Cr_2O_3, SrO, NiO, PbO, and Ac for the received material. The constituents of Malaysian molten slag depend on ores material and the process used for production; this type of molten slag was the byproduct of steelmaking slag using electric arc furnace. The acid washing method considerably affects the metal oxides of the molten slag. The increment of Fe_2O_3 content can be attributed to the depletion of CaO, ZnO, and SiO_2 in the washed molten slag affecting

Table 2. Pore characteristics of the molten slag.

Molten slag	Raw material	Acid washing method
BET surface area (m²/g)	3.04	0.85
Pore volume (cm³/g)	0.09	0.17
Average pore diameter (nm)	107.29	821.35

on increasing in the content of Fe_2O_3. The increasing of Fe_2O_3 and decreasing of CaO will improve the catalytic activity by increasing the acidity properties of modified molten slag as shown in Table 4. In addition, grinding molten slag before acid washing might increase the iron oxide content according to Shen & Forssberg [5], they ascribed increasing iron oxide to use the grinding machine.

Table 2 shows the surface area analysis in the raw molten slag (unmodified) and modified material. This result indicates significant change among the raw and modified material by acid washing method. The BET surface area of the raw material was 3.40 m²/g as shown in Table 2. This result is roughly consistent with Hocheng *et al.* [16] when they investigated EAF slag with the BET surface area of 2.68 m²/g. whereas, the BET surface area is considerably decreased during the acid washing method, it was 0.85 m²/g. This effect may attribute to HCl washing which dissolve some oxides and then deposit these oxides in the open pores or calcination after acid washing method which caused collapse of a portion of the pores caused by the process. Some pores also fuse and then forms larger holes, thereby decrease the specific sur-

face area. This is due to unstable material at higher temperature which is confirmed by Yildirim & Prezzi [17]. The authors stated the presences of unstable phases in slag's mineralogy, caused mainly by the presence of free CaO. When it reacted with water, free lime hydrated forming portlandite ($Ca(OH)_2$). The molten slag is classified as type of isotherm (III) as shown in Figure 2 (a) and (b). This result indicates significant change among the raw and modified material. This gap between equilibrium adsorption and desorption corresponds to the hysteresis. A hysteresis loop appears when capillary condensation occurs, in particular, when molecules on two opposing walls become sufficiently close to each other and collapse into thermodynamically low energy states. After reducing pressure during desorption, the molecules at low energy do not tend to leave their place; therefore, the same molecules are desorbed at low pressure [18]. The hysteresis loop for the Figure 2 (a) and (b), are considered to belong under type H3, which is characterized by the formation of plates from agglomerated particles. The result is in agreement with the SEM analysis Figure 3.
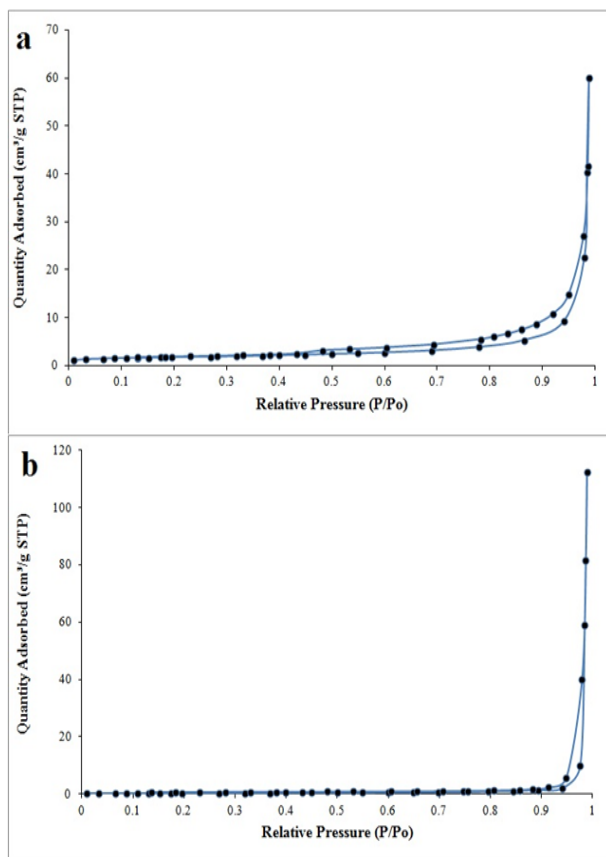

Figure 2. Isotherm of molten slag (a) raw material and (b) modified material.
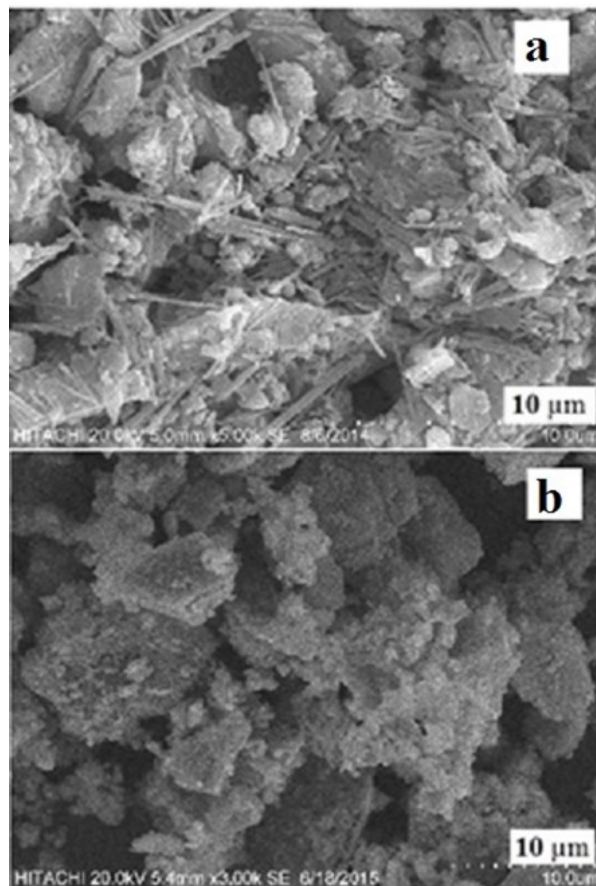

Figure 3. SEM morphology of molten slag (a) raw material and (b) modified material.

The catalyst surface concentrations of acidic sites was measured by temperature programmed desorption of ammonia (TPD-NH$_3$). The data obtained from the TPD-NH$_3$ profile of the raw material (Figure 4a) reveal that the acidic site is distributed in one region at temperature 702 °C with the total amount of gas adsorbed at about 159 µmol/g. Such result is attributed to the chemical bond involved in the electron sharing between the adsorbate and adsorbent. Moreover, this type of molten slag considers lower acidity properties due to high presence of CaO content as mentioned in Table 1. High amount of tricalcium silicate and lime (CaO) present in steel slag composition slightly reduced the acidity properties of the slag as reported by Shen & Forssberg [5], By contrast, the TPD spectra of material after washing with HCl (Figure 4b) shows a strong peak noted at 910 °C. Table 3 shows that the total amount of gas adsorbed is 1224 µmol/g. This result is achieved because the majority of the cations released from the ferrous slag samples after acid leaching is Ca, followed by Si, with little amounts of iron (Fe) [4].

3.2 Characterization of Bio-fuel

3.2.1 Functional group analysis of bio-fuel

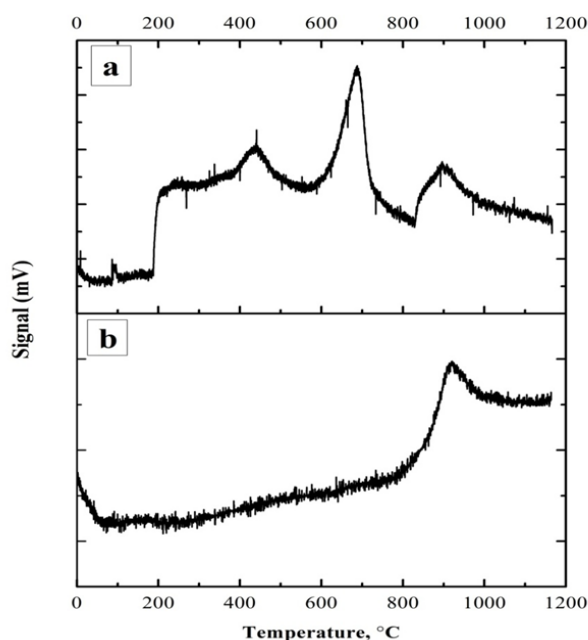To measure the catalytic performance of the catalyst, both raw and modified molten slag dross were applied in the pyrolysis of waste cooking oil together. The results were compared with non-catalytic pyrolysis of waste cooking oil as thermal cracking. FT-IR analysis was performed to examine the chemical functional groups present in the bio-fuel produced from the pyrolysis. An important observation on the bio-fuel 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 [19]. Figure 5 displays the comparison of main functional groups between waste cooking oil and bio-fuel produced using molten slag before and after modification. The pyrolysis oil (biofuel) 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 [20-22]. 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 molten slag 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-fuel indicates the presence of carboxylic acid in small amounts.
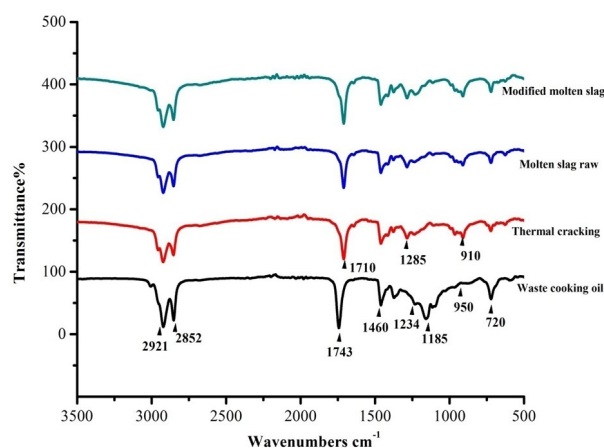

Figure 5. FT-IR spectra for WCO and bio-fuel product from thermal cracking, catalyzed for raw molten slag and modified molten slag.

Figure 4. TPD-NH$_3$ analysis for molten slag (a) raw material and (b) modified material.

Table 3. TPD-NH$_3$ analysis for Molten Slag (a) raw material and (b) modified material

Method	Raw material	Acid washing
Amount of gas adsorbed (µmol/g)	159	1224

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 4.

3.2.2 Chromatographic Analysis of the Bio-fuel

For obtaining a detailed understanding of the selectivity of raw and modified molten slag toward n-alkane and alkene obtained from catalytic pyrolysis, the composition was analyzed by GC analysis. Based on Hafriz *et al.* [23] the types of catalyst present would affect the selectivity in the liquid hydrocarbon product generated from catalytic pyrolysis of WCO. The catalyst was used as a control catalyst, was one of important commercial catalyst namely ZSM-5 [23]. It was successfully used to convert oxygenated organic compounds into hydrocarbons in pyrolysis of waste cooking oil due to their high acidity value and surface area [24-26].

ZSM-5 was calcined at 700 °C in a tubular furnace. The surface area was 55.8 m^2/g, pore volume of 0.96 cm^3/g and the acidity tested by TPD-NH$_3$ of 2077 µmol/g. The bio-fuel yield 28.25% from catalytic cracking by ZSM-5 as shown in Figure 6. While, the yield of bio-fuel produced from catalytic pyrolysis of waste cooking oil using modified molten slag showed the increment of 14.7% and 14.9%, respectively when compared to thermal cracking as shown in Figure 6. The thermal cracking of waste cooking oil not only gave low hydrocarbon yield (3.1%) but also poor product selectivity of the deoxygenized liquid hydrocarbon as shown in Figure 7. This shows that the catalytic pyrolysis is faster and more selective than thermal cracking by maximizing the production of liquid fraction as reported by Hafriz *et al.* [25]. Whereas, the modified molten slag significantly increased selectivity of n-C$_{15}$ to 30%, proving the catalytic reaction was promoted by modified catalyst. The result in agreement with Kar & Gurbuz [9] when they noticed the transition metal oxides in blast molten slag increased the degree of catalytic decarboxylation. For the
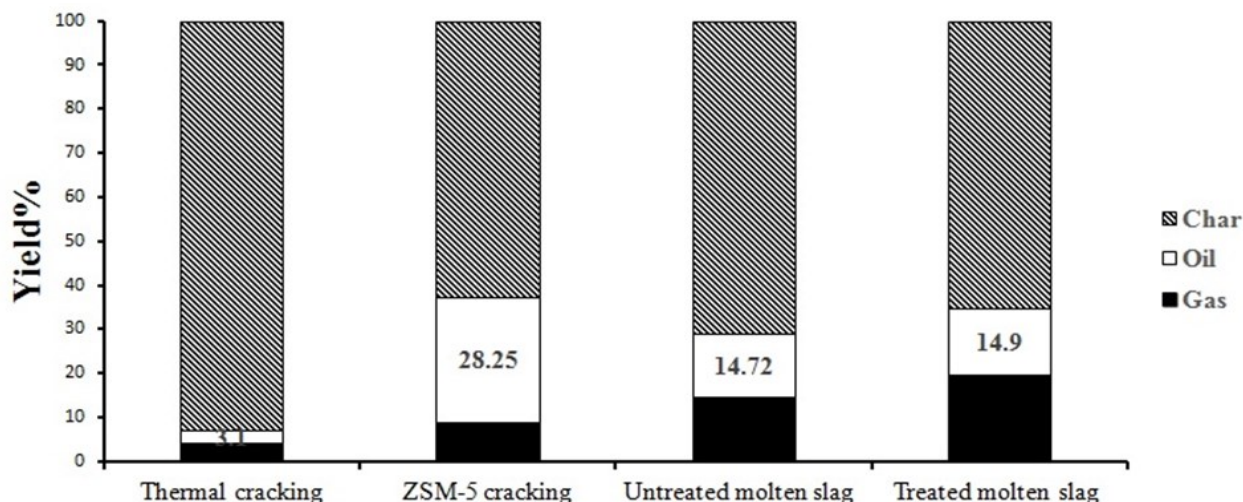

Figure 6. Yield percentage of bio-oil from catalytic pyrolysis.

Table 4. Summary of characteristic IR absorption for bio-fuel

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

molten slag used in this research, the XRF analysis revealed that it was ferrous slag type containing Fe_2O_3, CaO, and ZnO which are considered as important transition metals. Therefore, metal oxide content in this molten slag is being effective on the degrees of cracking process. Wang *et al.* [8] considered that Fe_2O_3 could play a significant role in promoting the cracking of hydrocarbons. In this study, it can be proven by higher conversion of WCO to liquid and gas products while using modified molten slag as mentioned in Figure 6. It can be suggested that the enhanced acidity of modified molten slag catalyst was due to increasing of Fe_2O_3 and decreasing of CaO which improve the activity of catalyst [8]. But, there is slightly increasing in the yield between the untreated and treated slag even though the acidity was increased from 159 to 1224 μmol/g in acid washing treatment as shown in Table 3.

The important notice in this catalytic pyrolysis of waste cooking oil, no soap have been found in bio-fuel produced for untreated and treated catalyst. Although, the steel slag are al-

kaline in nature according to Hocheng *et al.* [16]. Soap is created by hydrolysis (saponification) of a fat with alkali, so means there is no alkaline hydrolysis of fatty acid asters according to Maher & Bressler [19].

3.2.3 Reaction Pathway

The reaction pathway in Figure 8 was expected to be occurred based on composition of alkanes observed through gas chromatography (GC) analysis using alkane standards (C_7-C_{20}) and data provided by FTIR analysis. As mentioned in functional group analysis of biofuel, deoxygenation cracking reaction of WCO was involved due to removal of carbonyl group. Deoxygenation cracking of WCO using the catalyst comprised decarboxylation and decarbonylation reactions that occurred simultaneously, as illustrated in Figure 8. Decarboxylation removed carbonyl group in WCO to produce alkane by releasing CO_2 molecule. Meanwhile, decarbonylation eliminated carboxyl groups by releasing CO and H_2O to produce alkenes. Then the alkenes experienced oligomerization reaction to produce alkanes. This is in agreement with Hafriz *et al.* [25] and Hermida *et al.* [27] where the researchers reported that metal oxide catalyst acted as alternative deoxygenation cracking catalyst due to its acidity and basicity properties, in addition to its relatively high capacity in cracking oxygenated compound.

4. Conclusion

The characterization results of Malaysian molten slag shows that this material contains precious amount of metal oxides which exhibit cheap source of metals that commonly used as a catalyst. Surface area analysis, morphology of the surface, and acidity of the mentioned
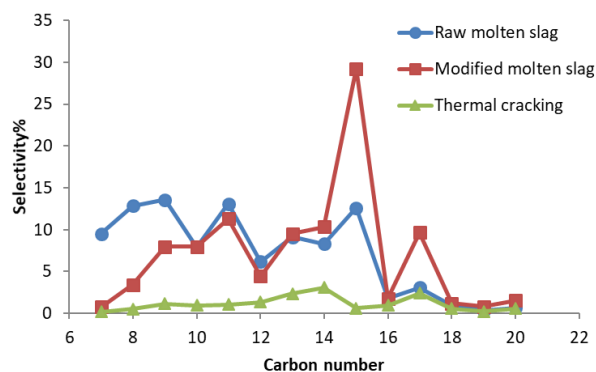
Figure 7. Selectivity of carbon number for raw and modified molten slag and thermal cracking.
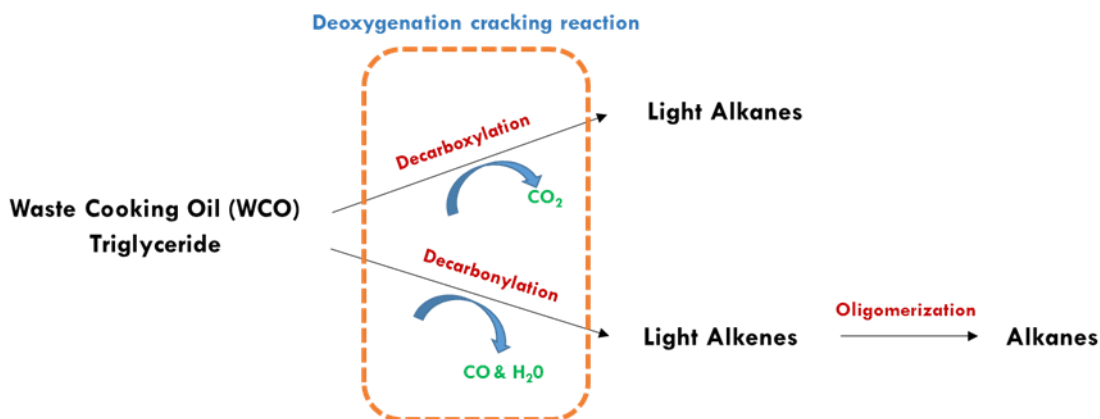
Figure 8. Deoxygenation cracking reaction of WCO over modified/unmodified molten slag catalysts to produce alkane product.

catalyst exhibited poor properties of the molten slag. The properties of the molten slag were changed by simple chemical activation using acid wash. One of the most important issue obtained from this study was the increase in the acidity of the treated molten slag. The performance of the selected material (molten slag) that used in pyrolysis of waste cooking oil exhibited modified molten slag as a good candidate in the cracking reaction.

Acknowledgments

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