

# Production of Biodiesel from In-situ Transesterification and Activated Carbon from Coffee Residues

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## GRAPHICAL ABSTRACT



Image of (a) biodiesel from spent coffee grounds (SCG) via *in-situ* transesterification (a) and (b) activated carbon from coffee residue of transesterification reaction

## ABSTRACT

Biodiesel helps reduce the emission of carbon monoxide, hydrocarbons and total particulate matters as compared with petroleum. Analysis biodiesel was prepared using four different concentration sulphuric acid,  $H_2SO_4$  that acts as catalyst. In-situ transesterification and determination of biodiesel production were performed using gas chromatography–flame ionization detector (GC-FID) and gas chromatography-mass spectrometer (GC-MS) and nuclear magnetic resonance spectroscopy ( $^1H$  NMR). Increased percentage concentrations of  $H_2SO_4$  impregnation with spent coffee ground (SCG) made a significant impact on the biodiesel yield. The percentage conversion of biodiesel for 5%, 10%, 15% and 20% wt.  $H_2SO_4$  calculated about 13.66%, 36.87%, 62.27% and 81.43% respectively. Then, the spent coffee ground's (SCG) residue after the in-situ transesterification were collected to prepare activated carbon (AC) via one step activation with potassium hydroxide (KOH) and carbonized at  $500^\circ C$  for 2 hours. The prepared AC was further characterised using Fourier Transformed Infrared, FTIR and Thermogravimetric analysis, TGA and the results obtained for both raw SCG and AC/KOH were compared to study the advantages of AC over raw materials. For raw SCG obtained infrared spectrum showed many absorption bands present in the raw SCG whereas some absorption spectrums were missing in AC which indicates some of the functional groups were volatilised during carbonisation process. In addition to this, TGA was also performed for both the raw SCG and AC/KOH and were compared to investigate the phase transformation or weight loss occurred before and after the preparation of AC. Thus, it can be concluded that biodiesel can be prepared from SCG and the AC from residue of transesterification method can be further used for various industrial use such as purification, separation and recovery.

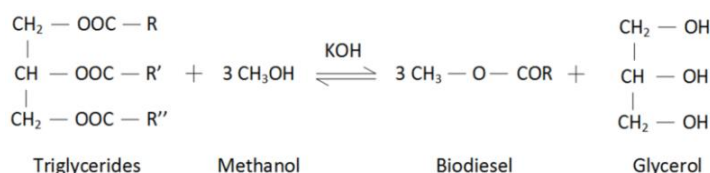
*Keywords: Biodiesel, spent coffee grounds, in-situ transesterification, activated carbon, one-step activation*

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## 1. INTRODUCTION

Due to diminishing crude oil reserves and alarming rate of global warming, many research programs regarding alternating energy are mostly focused on the development of green energy, renewable sources as well as environmentally friendly processes [1]. Therefore, Sophie Bendal have discussed that there is a rapid development in production of biodiesel from various sources such as palm oil, soybean oil, algae and vegetable oils. Being the main countries of resources of palm oil, Malaysia and Indonesia, the production of biodiesel is considered as replacement of the fossil fuels. Their current capacity for the production of biodiesel is approximately 42 billion liters [2].

The most commonly used method to synthesis biodiesel is by transesterification which is a process used to convert triglyceride by using short chain alcohols, usually methanol or ethanol to produce fatty acid alkyl esters and glycerol with the present of acid or base catalyst. The general reaction of this reaction is shown in Figure 1.



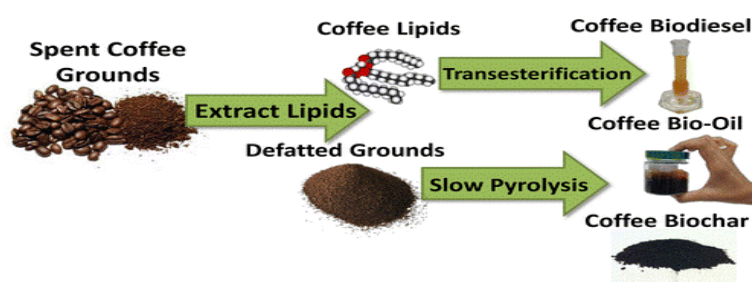
**Figure 1.** Transesterification of triglyceride with alcohol (Anuar and Abdullah,2016; Moreira *et al.*, 2013)

Carbon is traditionally obtained from petroleum coke, pitch and coal but these non-renewable sources had led to other alternative source like biomass [3]. There are a lot of researches concerning activated carbon in which they are using different source. Activated carbon is usually produced from biomass waste materials which is abundance after an industrial production or carbon-based organisms which are abundance in nature.

After the extraction of biodiesel from the spent coffee grounds, the remaining residue is considered a waste and to overcome this waste it was used to prepare high surface activated carbon with multipurpose and industrial use. Apart from purification, the activated carbon produced also can be used for separation, recovery processes, *etc.* Therefore, in this study, activated carbon from used coffee residue was produced through one-step activation using potassium hydroxide (KOH) as activating agent.

## 2. EXPERIMENTAL

This experiment was divided into two main stages. The first stage was the preparation of biodiesel from spent coffee grounds (SCG's) via *in-situ* transesterification with homogenous acid as a catalyst in methanol as a solvent. The second stage was preparation of activated carbon from the residue of in-situ transesterification via one-step activation with potassium hydroxide using carbonisation technique under 500°C for 2 hours. The synthetic route is presented in Figure 2. Both the biodiesel and prepared potassium hydroxide activated carbon (AC/KOH) were further proceeded for characterisation processes. The characterization techniques include Fourier transform infrared (FTIR) spectroscopy, thermal gravimetric analysis (TGA), gas chromatography (GC), and nuclear magnetic resonance (NMR).

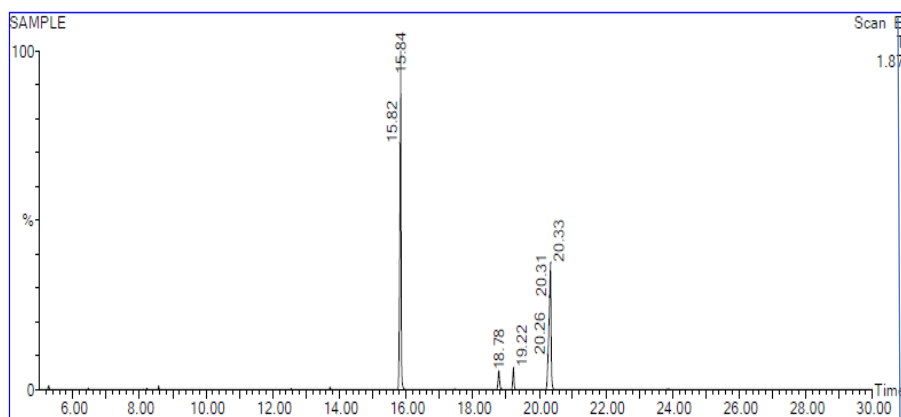


**Figure 2.** Synthetic route of biodiesel and activated carbon from SCG

## 3. RESULTS AND DISCUSSION

### 3.1. Characterisation of biodiesel

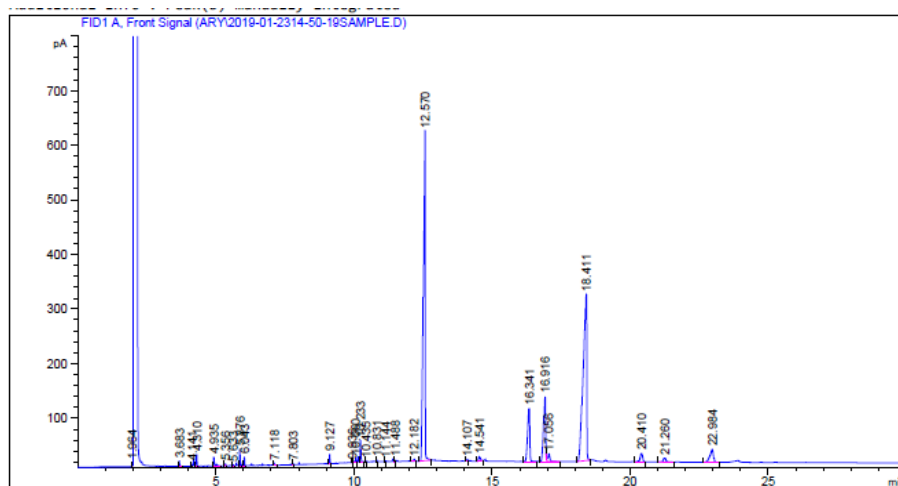
The biodiesel analysis using GC-MS was carried out to identify the fatty acid methyl esters (FAMES) composing the resulting biodiesel after the transesterification reaction. Since the chromatograms obtained from the all prepared catalyst shown a similar number of peaks and trend, thus 20 wt. %  $H_2SO_4$  was chosen for GC-MS analysis presenting all catalyst. Figure 3 shows the GC-MS spectrum for all the FAME present.



**Figure 3.** GC-MS spectrum for major FAME's present

The biodiesel obtained from the direct transesterification process was analyzed to investigate the effectiveness of impregnated 5%, 10%, 15% and 20% wt.  $\text{H}_2\text{SO}_4$  as catalyst to catalyze the transesterification reaction of SCG's with methanol. GC method was used for analysis and for the confirmation of the components in biodiesel produced. The biodiesel, which is fatty acid methyl esters (FAMES), was firstly analyzed by GC-FID in order to determine the more abundant FAME present.

In general, the elution order for FAME catalysed by all concentrations of  $\text{H}_2\text{SO}_4$  impregnation showed similar elution order and only four intense peaks were identified. The chromatogram displayed better peak shapes and separated very well. Some of the peaks could not be detected or identify probably because of their intensities are too low to be considered satisfactory. Figure 4 shows typical example of the GC chromatogram of the FAMES for SCG's impregnated with 20% wt.  $\text{H}_2\text{SO}_4$  and GC chromatogram of FAME for SCG's impregnated with 5% wt.  $\text{H}_2\text{SO}_4$  obtained from the in-situ transesterification reaction.



**Figure 4.** Typical GC chromatogram of biodiesel production using 20% wt.  $\text{H}_2\text{SO}_4$  catalyst

The difference in the intensity of FAME's present can be clearly deduced, and thus higher concentration of catalyst loading (20% wt.  $\text{H}_2\text{SO}_4$ ) produces biodiesel with higher FAME yield while low catalyst loading (5% wt.  $\text{H}_2\text{SO}_4$ ) produces biodiesel with very less FAME yield. Therefore, the most abundant FAME's present were methyl myristate (58.44%), methyl stearate (3.72%), methyl palmitate (2.03%) and methyl linoleate (37.84%). Percentage composition of FAME was calculated by its peak area using the internal normalization technique. The formula used as below [4]:

$$\% \text{ FAME} = \frac{\text{Peak area of FAME}}{\text{Total peak area of all FAMES}} * 100\%$$

The yield of biodiesel and types of FAMES produced from SCG's impregnated with various concentrations of sulphuric acid was determined in previous method using GC, thus this is further proved using  $^1\text{H}$  NMR. The ratio of peak area of the methoxy protons from methyl esters (singlet) at 3.7 ppm and that of  $\alpha$ -carbonyl methylene groups from fatty acid ester at 2.3 ppm (triplet) are used in calculation of percentage conversion of TG to FAME using the relationship in eqn. below:

$$\% \text{ Yield} = \frac{2A1}{3A2} * 100\%$$

where  $A1$  = area of triplet methoxy protons from methyl esters and  
 $A2$  = area of doublet methylene proton from the esters.

Figure 5 (a) 5%, (b) 10%, (c) 15% and (d) 20% wt.  $H_2SO_4$  shows the percent yield of biodiesel obtained which is 12.66%, 36.87%, 62.27% and 81.43% respectively. It can be observed that, as the concentration of catalyst loading increases, the percentage yield of biodiesel also increases.

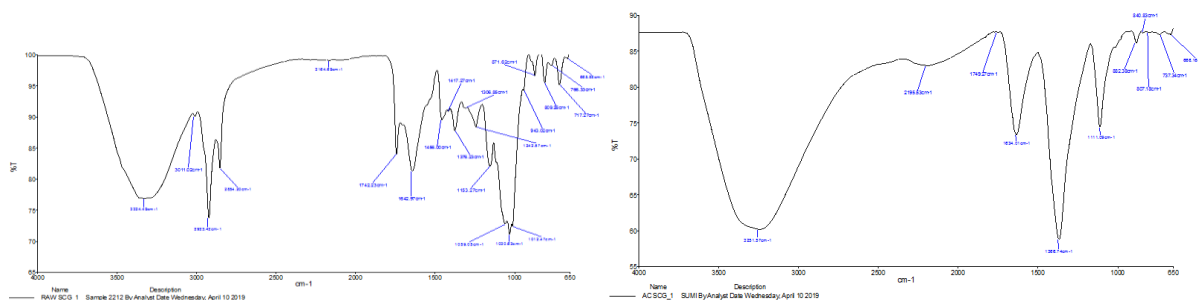


**Figure 5.** NMR spectra of (a) 5 wt.%, (b) 10 wt.% and (c) 15 wt.% of  $H_2SO_4$

### 3.2. Characterization of Activated Carbon

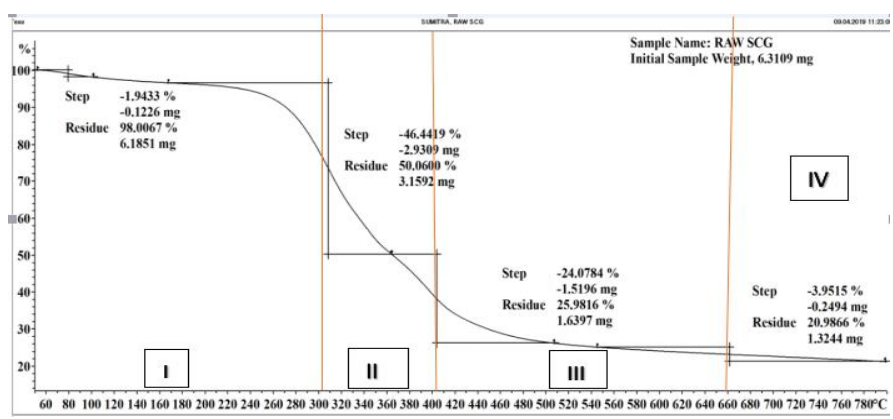
The prepared AC/KOH from the residue after the in-situ transesterification were examined by FTIR-ATR at wavelength between  $650$  and  $4000\text{ cm}^{-1}$ . The result obtained was compared with the infrared spectrum obtained for the raw SCG later on, so that the difference in phase transformation as well as the number of functional groups between both the spectrum of raw SCG and AC was analysed. Figure 6 shows the spectra of (a) raw SCG and (b) prepared AC/KOH from in-situ transesterification residue. The spectrum for prepared AC/KOH from in-situ transesterification residue the band,  $6251.57\text{ cm}^{-1}$  that refers to O-H hydrophilic group is still observed. In contrast, the bands in  $\sim 2900\text{-}2800\text{ cm}^{-1}$  which is C-H hydrophobic group appears only in the raw coffee waste. In activated carbon made from residue after

transesterification, the main surface functional groups present were carbonyl groups for ethers and phenols, therefore it is more intense in AC/KOH prepared. The spectra of C-O for ester, ethers or phenol are at  $1111.09\text{ cm}^{-1}$  and the C=C absorption band for aromatic compound are at  $1366.74\text{ cm}^{-1}$ . There are more absorption bands in raw SCG compare to the prepared activated carbon. The adsorption peak in this activated carbon spectrum was less than the raw SCG spectrum as the functional group disappeared after calcination. This shows the activation process takes places where all the disappeared functional group were evaporated as volatile materials as heat was applied to the sample. This process was called carbonization process. Finally, the carbonization of the material effect can be observed in the fact that the band in  $\sim 2900\text{-}2800\text{ cm}^{-1}$  almost disappears. It should be noticed a band in  $\sim 1000\text{ cm}^{-1}$  present in the raw SCG spectrum and not present in the other spectra. This band suggests the presence of a C-N bond, since the amount of nitrogen in raw SCG is three times higher than the amount in prepared AC/KOH [5].



**Figure 6.** FTIR spectra of (a) SCG and AC/KOH

TGA analysis was performed to the prepared AC in order to detect the effect of the one step chemical activation with KOH on the mass loss. Figure 7 shows the TGA thermogram of (a) raw SCG and (b) AC/KOH prepared from the residue of in-situ transesterification reaction and it has been separated into three different stages of I, II, and III. Stage I of the TGA thermogram above deduce about the mass loss of AC prepared as a result of dehydration. About 4% of weight loss occurred at temperature ranging between  $60\text{-}165^\circ\text{C}$  attributed to the elimination of water adsorbed physically in the mesopores and micropores [6]. The dehydration process occurred in relatively low temperature as compared to the weight loss occurred for the raw SCG. The second weight loss occurred at stage II where about 9%, occurring between  $170\text{-}710^\circ\text{C}$  corresponds to the decomposition of easily volatile materials as well as cellulose. At stage III where temperature range between  $715\text{-}800^\circ\text{C}$  weight loss, 37% that corresponds to the decomposition of lignin occurs for AC. In contrast to the TGA curve obtained for raw SCG, for AC there was no formation of ash occurs [7]. This is because ash content can lead to increase in hydrophilicity and can have catalytic effects, causing restructuring process during regeneration.



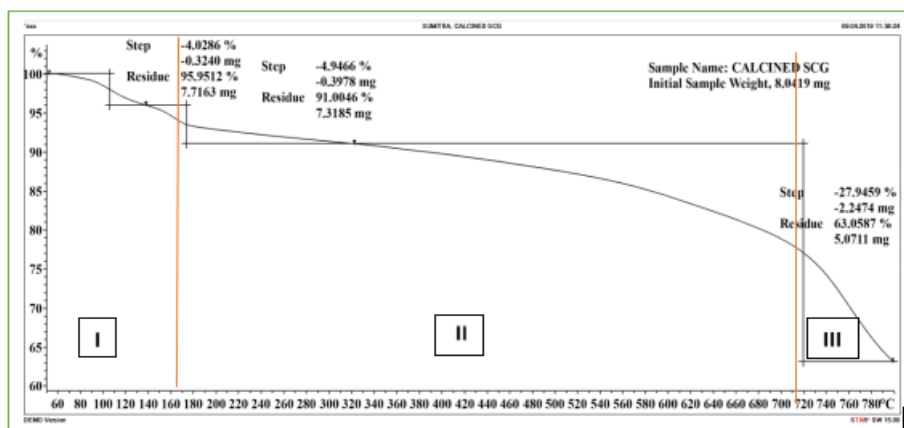


Figure 7. TGA curves of (a) raw SCG and (b) AC/KOH

#### 4. CONCLUSION

Biodiesel was successfully obtained from spent coffee grounds (SCG) via *in-situ* transesterification method using SCG impregnated with various concentration of sulphuric acid. The percentage conversion of biodiesel for 5% wt. H<sub>2</sub>SO<sub>4</sub>, 10% wt. H<sub>2</sub>SO<sub>4</sub>, 15% wt. H<sub>2</sub>SO<sub>4</sub> and 20% wt. H<sub>2</sub>SO<sub>4</sub> were 12.66%, 36.87%, 62.27% and 81.43% respectively. The optimum percentage conversion was obtained from 20% wt. H<sub>2</sub>SO<sub>4</sub>. Moreover, the highest amount of FAME's present in the obtained biodiesel were methyl myristate, methyl stearate, methyl palmitate and methyl linoleate where the percentage compositions were 58.44%, 3.72%, 2.03% and 37.84% respectively. AC was successfully prepared via the one step activation with KOH and carbonized at 500°C for 2 h. This was proven from the FTIR-ATR result as all main functional group which was hydroxyl group, carbonyl group, C=C stretching and C-H bending for aromatic compound were present. The prepared AC/KOH was identified and could be used effectively in various industrial use such as purification, separation, recovery and so on.

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