

Bio-Oil Upgrading to High Energy Biofuel by Olefination

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Abstract-Raw bio-oil produced by fast pyrolysis consists of a complex mixture of various oxygenated compounds which prevent its use directly as a fuel. The objective of this research is to improve the bio-oil quality. In this paper, we employed an olefination process to the raw bio-oil to produce a high-energy biofuel. Three alcohol treatments: 1-butanol alone, 1-octanol alone and a 1-butanol+1-octanol mixture with 1-octene as the olefin were added to react with raw bio-oil via olefination to produce a high-energy olefinated bio-oil fuel. The olefinated organic fraction obtained by utilizing 1-butanol+1-octanol mixture produced a higher yield and better quality boiler fuel compared to 1-butanol and 1-octanol alone. The olefinated organic fraction had an acid value of 23.3 mg KOH/g representing a reduction of 74.8% of the raw bio-oil acid value of 92.4 mg KOH/g. Compared to raw bio-oil the olefinated organic fraction of the 1-butanol+1-octanol mixture produced a higher heating value increase of 117.5% from the original 16.0 MJ/kg for raw bio-oil to 34.8 MJ/kg; the water content of the olefinated product decreased by 87.3% and oxygen content decreased by 64.3%. The olefination of the bio-oil was confirmed by GC-MS and FTIR. Our approach presented in this paper produced boiler fuel with improved quality compared to the previous researchers by reducing the consumption of alcohol solvent and reaction time.

Index terms: Bio-oil, Fast pyrolysis, Biofuel, Olefination, Higher heating value, GC-MS, FTIR.

I. INTRODUCTION

Bio-oil is typically produced by fast pyrolysis of biomass at 400 to 550 °C in the absence of oxygen. The yield of bio-oil is relatively high at 60-70% dry-weight basis or higher. Bio-oil is a dark brown colored liquid with pungent phenolic odor [1-3]. As a fuel raw bio-oil has environmental advantages when compared to fossil fuels because on combustion, bio-oil produces half the NO_x, negligible quantities of SO_x emissions and it is CO₂ neutral when compared to petroleum fuels [4, 5]. Bio-oil is very complex in chemical composition and contains large numbers of organic compounds such as carboxylic acids, aldehydes, ketones, alcohols, phenols and phenolic derivatives and others. The chemically complex mixture of bio-oil results in each separate bio-oil containing over 200 different organic compounds although over 400 organic compounds have been identified over the range of bio-oils produced [1,3,5]. The presence of oxygenated compounds results in typical bio-oil oxygen content of 40-50 wt%. Due to the presence of a high percentage of oxygen, raw bio-oils demonstrate some negative properties such as high water content, lower energy density,

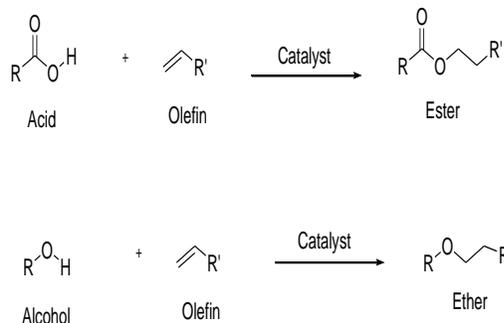
high acidity, immiscibility with petroleum products and viscosity increase over time [5-9].

Raw bio-oils are acceptable as boiler fuels and American Society for Testing and Materials (ASTM) D7544 10 Standard Specifications for Pyrolysis Liquid Boiler Fuel provide quality standards. The bio-oil boiler fuel quality is determined by ASTM D7544 10 by level of water content, viscosity and higher heating value (HHV). With the use of raw bio-oils as boiler fuels, requires it is treatment to improve the current boiler fuel quality, which eventually results in improvement of market acceptance and speed up commercialization [10].

The present methods for upgrading bio-oil to boiler fuel are based on catalytic esterification and olefination reactions. By these methods total oxygen removal is not required; moreover the retained boiler fuels produces high-energy organic fuels which are combustible and stable oxygenated compounds such as esters, acetals and ethers [11-13].

Esterification is a chemical process to convert the carboxylic acids present in bio-oils to esters, acetals and ethers by reacting them with alcohols in the presence of an acid or base catalyst. Researchers have proved that esterification via alcohol addition will reduce the acidity of the bio-oil, thereby improving the quality and stability of bio-oil [14-17]. Researchers have also tested alkaline, resin acid, super critical fluid technology and solid acid catalysts for bio-oil esterification. Bio-oil esterification methods have been tested with various parameters such as alcohol types and percentages, catalysts types, and reaction conditions [18-21].

The olefination reaction is one of the potential chemical processes to produce mainly esters and ethers by reacting olefin with carboxylic acids and aldehydes in the presence of alcohol as a solvent and co-reagent. The olefination reaction scheme is shown below in Scheme 1. This reaction produces mainly esters with a maximum HHV of 23-31.9 megajoule per kilogram (MJ/kg), and considerably reduces the oxygen content. Therefore, esterified or olefinated bio-oil is appropriate heating fuel, however, not suitable transportation fuel [12,13,18,22,23].



Scheme 1. Olefination reaction pathway [12,13,22].

Steele *et al.* applied for a patent on olefination of bio-oil to produce a high-energy boiler fuel. The Steele *et al.* (2011) olefination/esterification experiment was performed by addition of bio-oil (85.7%), butanol (28.6%), and 1-octene (14.3%) with 5 wt% of heterogeneous acidic catalyst at a temperature of 250 °C with pressure of 100 psi helium for 2 hr of reaction time. The patent application also disclosed olefination of bio-oil utilizing 1-butene gas as the olefin source by addition of bio-oil, butanol and gaseous 1-butene at 30 psi of pressure with 5 wt% of acid catalyst at a temperature of 250 °C with pressure of 100 psi helium. For the liquid embodiment to produce olefinated/esterified bio-oil the inventors showed that HHV increased from 17.20 to 32.80 MJ/kg, water content decreased from 28.60 to 6.0 wt% [12].

Zhang *et al.* (2011) studied the sulfonic acid resin catalytic olefination of bio-oil (1.5 g) with 1-octene (0.25 g or 16.7%) with addition of 1-butanol addition ranging from 0.25 to 0.75 g (16.7 to 50%) reacted at a temperature ranging from 80 to 150 °C for a reaction time of 3 h. This treatment resulted in an olefinated product with lower acidity (pH value increased from 2.5 to >3.5), reduction of water content 37.2 to less than 7.5% and an increase in HHV to 30.0 MJ/kg from the bio-oil HHV of 12.6 MJ/kg [23].

Zhang *et al.* (2013) tested the upgrading of bio-oil with the olefins cyclohexene, 1,7-octadiene and 2,4,4-trimethyl pentene along with 1-octene and iso-butanol, t-butanol, and ethanol and 1-butanol as solvents. The Zhang *et al.* performed the olefination reaction in the presence of silica sulfuric acid catalyst at 120 °C for a time of 3 h. Better results were obtained with 1-butanol/1-octene consisting of 0.75 g (50%) 1-butanol and 0.6 g (40%) 1-octene. For this olefinated product acidity was lowered (pH value increased from 2.5 to >3.5), water content decreased from 37.2 to nearly 7% and the HHV value increased from 12.6 MJ/kg to about 31.9 MJ/kg [13].

Chatterjee *et al.* (2013) explored the olefination of bio-oil using 1-octene as the olefin and ethanol as the alcohol. They reported that ethanol was not as effective as 1-butanol for promoting 1-octene and bio-oil phase compatibility [22]. Zhang *et al.* 2011 and 2013 and Chatterjee *et al.* 2013 performed their experiments at a micro scale with a high percentage of alcohol and reaction time was relatively long at 3 hr [23]. The objective of our current study is to produce a higher-energy olefinated

bio-oil useable as boiler fuel with higher HHV and lower acid value (AV) with a shorter reaction time than attained by previous researchers.

II. MATERIALS AND METHODS

1-butanol, 1-octanol and 1-octene were obtained from Sigma Aldrich. Nickel on silica-alumina (Ni/SiO₂-Al₂O₃) and potassium carbonate (K₂CO₃) were obtained from Alfa Aesar. The bio-oil required for this study was produced with the Mississippi State University (MSU) fast pyrolysis auger reactor located in the Department of Sustainable Bioproducts. The feedstock utilized was clear pine wood particles of 1-3 mm

diameter at a moisture content of 8-10% (dry-weight basis) with 65% yield. Raw bio-oil (RBO) was produced by the fast pyrolysis process performed at a temperature of 450 °C with nitrogen carrier gas at a rate of 7 kg/h and with yield of 65% [1]. All described chemicals were used with no further purification.

All olefination experiments were performed in a stainless steel, high-pressure batch autoclave reactor equipped with an overhead magnetic stirrer, a pressure indicator with a maximum capacity of 5000 psig and a thermocouple for temperature monitoring in the range of 0-500 °C. The autoclave was equipped with an electrical heating and cooling system to control the temperature inside the reactor. The olefination reaction was applied to RBO by addition of an alcohol, olefin and olefination catalyst.

For this study we tested 1-octene as the olefin with 1-butanol (BtOH), 1-octanol (OtOH) and 1-butanol+1-octanol (BtOH+OtOH) mixture as the alcohol solvents; the catalyst was a mixture of Ni/SiO₂-Al₂O₃ (3 wt%) and K₂CO₃ (5 wt%). Olefination reactions were performed by addition of BtOH (30 wt%) alone, OtOH (30 wt%) alone and the combination of the BtOH+OtOH (30 wt%) mixture (this mixture was prepared by physical addition of 1:1 BtOH and OtOH, i.e., 15 wt% of each) to RBO by using a common 1-octene (10 wt%) as an olefin and a mixture of Ni/SiO₂-Al₂O₃ (3 wt%) and K₂CO₃ (5 wt%) as the catalyst. For the three alcohol solvents a reaction temperature of 250 °C was applied without pressure while being stirred for 90 min.

Following each reaction described above, the reactor was cooled to room temperature and vented to atmospheric pressure. The product from the reaction was collected and the two liquid layers, olefinated organic fraction (OOF) and aqueous fraction were separated by centrifugation for 2-4 hr at 4000 rpm. The resultant two phases were removed by separating funnel and yields of all phases and products were calculated.

The alcohol solvent that produced the best qualities and yield of OOF was then chosen for further testing of reaction temperatures and times. The reaction temperatures applied to the solvent selected as the most promising were 225, 250 and 275 °C; reaction times applied were 60, 90 and 120 min, respectively. Again no pressure was applied during the reaction.

The temperature that produced the best qualities and yield of OOF for the tested best alcohol solvent was then identified.

At this temperature reaction times were varied for 60, 90 and 120 min. Again, the reaction time that produced the best qualities and yield of OOF was selected as the optimum time among those tested.

The RBO and OOFs were characterized using the following ASTM methods. The acid value (AV)s were determined by ASTM D664 method which comprised of dissolving 1 g of bio-oil in 50 ml of 35:65 ratio of isopropanol to water mixtures and titrating to a pH of 8.5 with 0.1N KOH solution. The HHVs were determined by Ika-5000 bomb calorimeter by ASTM D240. Water content was determined by Karl-Fisher titration by ASTM E203. Elemental carbon, hydrogen, and nitrogen were determined by EAI CE-440 elemental analyzer with oxygen content determined by difference according to ASTM D5291. The best OOF measured in terms of higher yield and better quality was analyzed by gas chromatography–mass spectrometry (GC-MS) and Fourier transform infrared spectroscopy (FTIR).

III. RESULTS AND DISCUSSION

The olefination process was applied to the RBO to produce an OOF product with low AV, high HHV and less water content suitable for boiler fuel. **Table 1** compares AV's, HHV's and water contents of the OOFs obtained from three alcohol

treatments. **Table 1** indicates that olefination of RBO with BtOH alone the AV decreased from 92.4 mg KOH/g for raw bio-oil to 31.6 mg KOH/g, a decrease of 64.7%. For the combination of BtOH+OtOH mixture the AV decreased from 92.4 mg KOH/g for raw bio-oil to 23.3 mg KOH/g, a reduction of 74.8%. For OtOH alone the AV decreased from 92.4 mg KOH/g for raw bio-oil to 25.4 mg KOH/g, a decrease of 72.5%.

As shown in the **Table 1**, olefination of the RBO with BtOH alone resulted in a HHV nearly twice as high for OOF with an increase from 16.0 MJ/Kg to 32.5 MJ/Kg, an increase of 103.0%. For the olefination of RBO with the combined BtOH+OtOH mixture the HHV gains more than doubled for the OOF with an increase from 16.0 MJ/Kg to 34.8 MJ/Kg, an increase of 117.5%. For the olefination of RBO with OtOH alone the HHV also more than doubled for the olefinated bio-oil product with an increase from 16.0 MJ/Kg to 34.9 MJ/Kg, an increase of 118.1%. The **Table 1** also shows the water content of the OOF from the OtOH alone treatment was reduced to 6.9 wt% compared to 30.6 wt% for raw bio-oil, a decrease of 77.4%. The OOF obtained from the BtOH+ OtOH mixture treatment had a water content of 3.9 wt% compared to 30.6 wt% for raw bio-oil, this was a decrease of 87.3%. The water content of the OOF from the addition of OtOH alone was reduced to 2.2 wt% compared to the 30.6 wt% for raw bio-oil, a decrease of 92.8%.

Table 1. Comparison of AV, HHV, water content between RBO and OOFs obtained from BtOH alone, OtOH alone and BtOH+OtOH mixture with 1-octene as olefin treatments.

Property	RBO	BtOH	BtOH+OtOH	OtOH
AV, mg KOH/g	92.4	31.6	23.3	25.4
HHV, MJ/kg	16.0	32.5	34.8	34.9
Water content, wt%	30.6	6.9	3.9	2.2

Figure 1 compares the elemental analysis results measuring carbon, hydrogen, nitrogen and oxygen content (C,H,N,O) of the OOF products produced from treatments (by addition of BtOH alone, OtOH alone and BtOH+OtOH separately) with 1-octene as olefin to that of RBO. The OOF produced from the BtOH alone treatment carbon content increased to 69.5 wt% from 38.4 wt% from that of RBO, an increase of 80.9%. The hydrogen content of OOF from BtOH increased to 10.5 wt% from 7.6 wt% of RBO, an increase of 27.6%. The nitrogen content of OOF from BtOH alone treatment decreased from 0.2 wt% for RBO to 0.1 wt%. The oxygen content of OOF produced from the BtOH alone treatment reduced by 62.9% from RBO of 53.7 wt% to 19.9 wt%.

The carbon content of the OOF obtained from BtOH+OtOH mixture treatment increased to 69.5 wt% from 38.5 wt% of

RBO, an increase of 80.5%. Hydrogen content was 26.9% higher for the OOF produced from combined BtOH+OtOH with the value of 10.4 wt% compared to the 7.6 wt% of RBO. Nitrogen decreased from 0.2 wt% for RBO to 0.1 wt%. Oxygen content of OOF from this combined alcohol treatment reduced by 64.3% from 53.7 wt% of RBO to 19.2 wt%.

As shown in **Figure 1**, the carbon content of the OOF produced from OtOH alone increased to 71.0 wt% from 38.5 wt% of RBO, an increase of 84.4%. The hydrogen content increased to 10.1 wt% form 7.6 wt% of RBO. Nitrogen content decreased from 0.2 wt% of RBO to 0.1 wt% for the OOF from OtOH alone treatment. Oxygen content of OOF from OtOH alone treatment reduced by 65.0% from 53.7 wt% of RBO to 18.8 wt%.

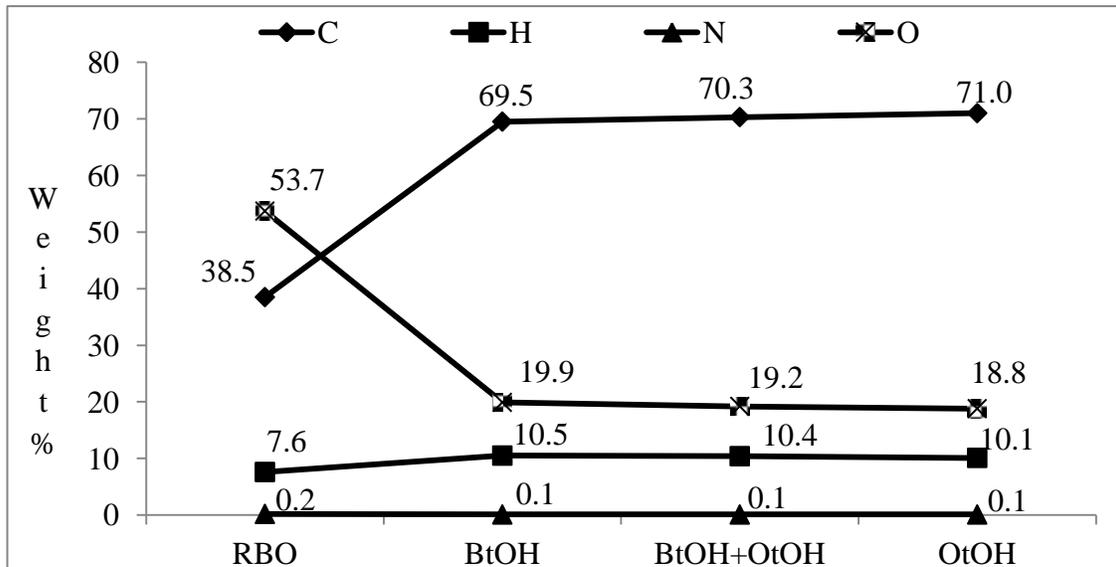


Figure 1. Comparison of C, H, N, O weight percentages between RBO and OOF products obtained from BtOH alone, OtOH alone and BtOH+OtOH mixture with 1-octene as olefin treatments.

Figure 2 compares the OOF, water, char and gas yields obtained from the olefination of the RBO with three (BtOH alone, OtOH alone and BtOH+OtOH mixture as a solvent) alcohol treatments. As shown in Figure 2, the mixture of BtOH+OtOH as a solvent treatment produced a higher yield of OOF product and lower water (aqueous fraction) and gas yields compared to BtOH alone and OtOH alone treatments. The BtOH+OtOH as a solvent treatment produced 13.3% and 6.5% higher yield of OOF compared to the BtOH and OtOH treatments, respectively.

275 oC at an interval of 25 oC by following the procedure described in section 2.2

Among all three runs, BtOH+OtOH mixture as an alcohol solvent treatment produced an OOF with higher yield and improved characteristics in terms of reduced AV, higher HHV, lowered water and oxygen content. The OtOH alone treatment produced a very small improvement in the reduction of water content and oxygen reduction. However, the lower yield and high utilization of OtOH (30 wt%) is a much more expensive treatment compared to the mixture of BtOH (15 wt%)+OtOH (15 wt%). Therefore, the OOF obtained from the combined BtOH+OtOH mixture with 1-octene treatment was considered as the best treatment to produce maximum OOF yield. For this (BtOH+OtOH mixture as an alcohol) best treatment, the effect of the reaction temperature was studied. The olefination reactions were conducted at a temperatures ranging from 225-

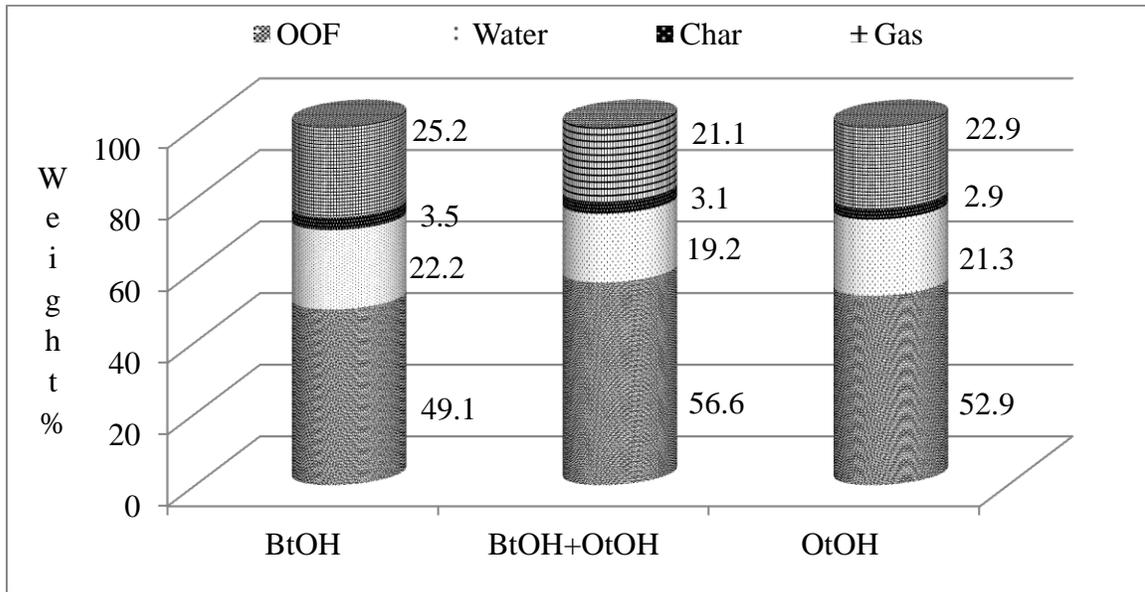


Figure 2. Comparison of OOF, water, char and gas yields obtained from BtOH alone, OtOH alone and BtOH+OtOH mixture with 1-octene as olefin treatments.

Figure 3 shows the effect of reaction temperature on the olefination of RBO by combined BtOH+OtOH as an alcohol solvent treatment. Figure 3 shows the HHVs, AVs, water content (H₂O), oxygen content (O₂) and OOF yield of the three treatments at a temperature 225 °C, 250 °C and 275 °C. As shown in the Figure 3, the olefination reaction performed at 250 °C produced a 55.8 wt% of higher yield of OOF compared to the treatments at 225 °C with 54.5 wt% yield and at 275 °C with 53.1 wt% yield. The HHV's of all the three treatments had approximately the same values at 34.6, 34.8 and 35.0 MJ/kg at 225 °C, 250 °C and 275 °C, respectively. The AVs of the OOFs produced at 225 °C, 250 °C and 275 °C were 30.1, 23.3 and 21.2 mg KOH/g, respectively. The water content of the OOFs produced at 4.5, 3.9 and 3.7 wt% for the respective treatment temperatures of 225, 250 and 275 °C. The oxygen content of the OOF produced at 225, 250 and 275 °C were 20.7, 18.8 and 18.7 wt%, respectively.

The OOF produced at 250 °C treatment had 22.6% lower AV, 0.6% higher HHV, 13.4% lower water content, 9.2% less oxygen content and 2.4% higher OOF yield when compared to the 225 °C treatment. Comparing the OOF products produced at 250 °C and 275 °C treatments OOF produced at 275 °C had 9.0% lower AV, 0.6% higher HHV, 5.1% lower water content, 0.5% less oxygen content and 5.1% lower OOF yield when compared to the treatment 250 °C. Among these three runs, the olefination reaction performed at 250 °C produced a higher yield of OOF compared to the 225 °C and 275 °C treatments. The effect of the reaction time on the olefination of the RBO was also studied at an optimized reaction temperature of 250 °C. The olefination reactions were conducted with a reaction time in the range of 60-120 min at an interval of 30 min at a temperature of 250 °C by following the procedure described in section 1.2.

The effect of reaction time on the olefination of RBO by combined BtOH+OtOH as an alcohol solvent treatment is shown in the Figure 4. The olefination reactions were performed as mentioned in section 2.2 at three different time intervals in the range of 60-120 min at a temperature of 250 °C and without external pressure. Figure 4 shows the HHV, AV, O₂ and OOF yield of the three treatments performed at 60, 90 and 120 min reaction time intervals. As shown in the Figure 4, olefination reaction performed at 250 °C with reaction time for 90 min produced with 55.8 wt% of higher yield of OOF compared to the 51.7 wt% and 47.0 wt% OOF yields at reaction time 60 and 120 min, respectively. The HHV's of the OOF produced with reaction time 90 min had higher value of 34.8 MJ/kg compared to 33.0 MJ/kg at 60 min and 34.2 MJ/kg at 120 min of time intervals. The AV of the OOF produced at 90 min was contained 23.3 mg KOH/g; whereas both the OOF products produced at 60 min reaction contained 28.0 mg KOH/g and 120 min reaction contained 27.1 mg KOH/g higher AV compared to 90 min reaction time OOF product. The O₂ content of the OOF produced with 60 min of reaction time had 20.0 wt% and OOF's produced at 90 min and 120 min of time intervals of reaction time have approximately same O₂ of 18.8 wt% and 18.4 wt%, respectively.

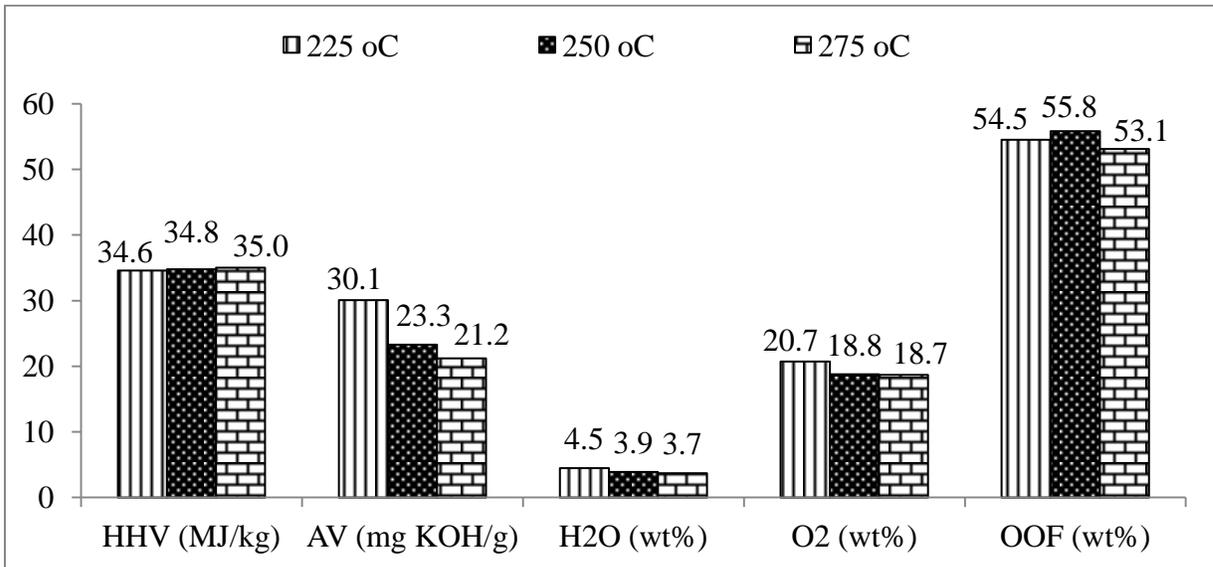


Figure 3. Effect of reaction temperature on the olefination of RBO by combined BtOH+OtOH mixture as an alcohol solvent treatment.

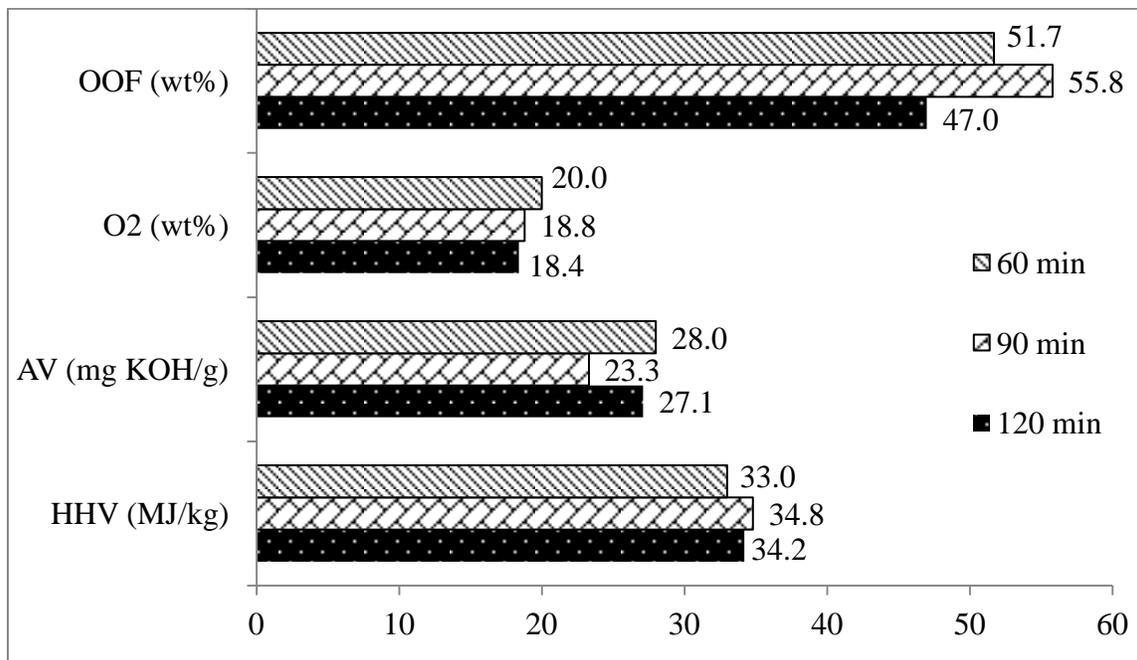


Figure 4. Effect of reaction time on the olefination of RBO by combined BtOH+OtOH as an alcohol solvent treatment performed at 250 °C.

The boiler fuel produced with our process had HHV of 34.8 MJ/Kg energy density which is higher than the boiler fuels produced by previous researchers. The olefination reaction time was reduced by 50% from 3 hr to 1.5 hr compared to the previous research methods. The consumption of alcohol was also reduced considerably by over 50 wt%. The oxygen and

water content of the boiler fuel also reduced to 18.8 wt% and 3.9 wt%, respectively. Overall, our approach presented in this paper produced boiler fuel with improved quality compared to the many previous researchers Steele et al. (2011), Zhang et al. (2011), Zhang et al. (2013) and Chatterjee et al. (2013).

1.1. GC-MS analysis

Table 2 shows chemical composition comparison of the RBO and OOF produced from mixed alcohol (BtOH+OtOH) as a solvent treatment by GC-MS analysis. From Table 2 it is observed that there is large difference between RBO and olefinated product chemical composition after the olefination reaction. As shown in Table 2, RBO contains mostly oxygenated compounds in the form of alcohols (34.3%), aldehydes and ketones (34.1%), ester and ethers (12.1%), carboxylic acids (15.7%) and others (3%). Presence of all these

compounds is attributed to the negative properties of the raw bio-oil. Compared to RBO an olefinated bio-oil contains less alcohol (24.4%) and ketones (1.9%); ester and ethers (26.7%), carboxylic acids (5.2%) and others (3%) were observed to decrease. The reduction of acid content was 66.9 area%. The increase of esters and ethers were observed to be by 120.7 area%. In Table 1 the previously discussed decrease in OOF AV compared to that of RBO is also in good agreement with the conversion of carboxylic acids to esters and other oxygenates as shown in Table 2 GC-MS results.

Table 2. The chemical composition of the RBO and OOF produced from BtOH+OtOH as a solvent treatment at 250 °C for 1.5h.

Components	RBO (Area %)	OOF (Area %)
Acids	15.7	5.2
Esters & Ethers	12.1	26.7
Aldehydes & Ketones	34.1	1.9
Alcohols	34.3	24.4
1-Octene	0	21.3
Other	3	1.3

1.2. FTIR spectral analysis

Figure 5 compares FTIR spectral data between the RBO and OOF produced from BtOH+OtOH treatment. Characteristic vibrational modes are observed at 3200-3600 cm⁻¹ (OH stretching), 2830-2950 cm⁻¹ (CH stretching, aliphatic), 1650-1710 cm⁻¹ (C=O stretching) and 1375-1475 cm⁻¹ (C-H vibrations). From Figure 5, it is evident that following olefination the OH stretching absorption peak of OOF was decreased due to the conversion of oxygenated compounds such as carboxylic acids, water and alcohols present in the RBO. The increase of the C=O and C-O stretching peak indicates the presence of ester and ether oxygenated compounds present in the OOF. The increase in intensity of C-H aliphatic stretching (2830-2950 cm⁻¹) absorption peak of OOF compared to the RBO spectra indicates the formation of ethers, esters (butyl and octyl) and acetals. The FT-IR spectral data shown in Figure 5 is in good agreement with the GC-MS spectral properties shown in Table 3 and physical and chemical properties as shown in **Table 1**.

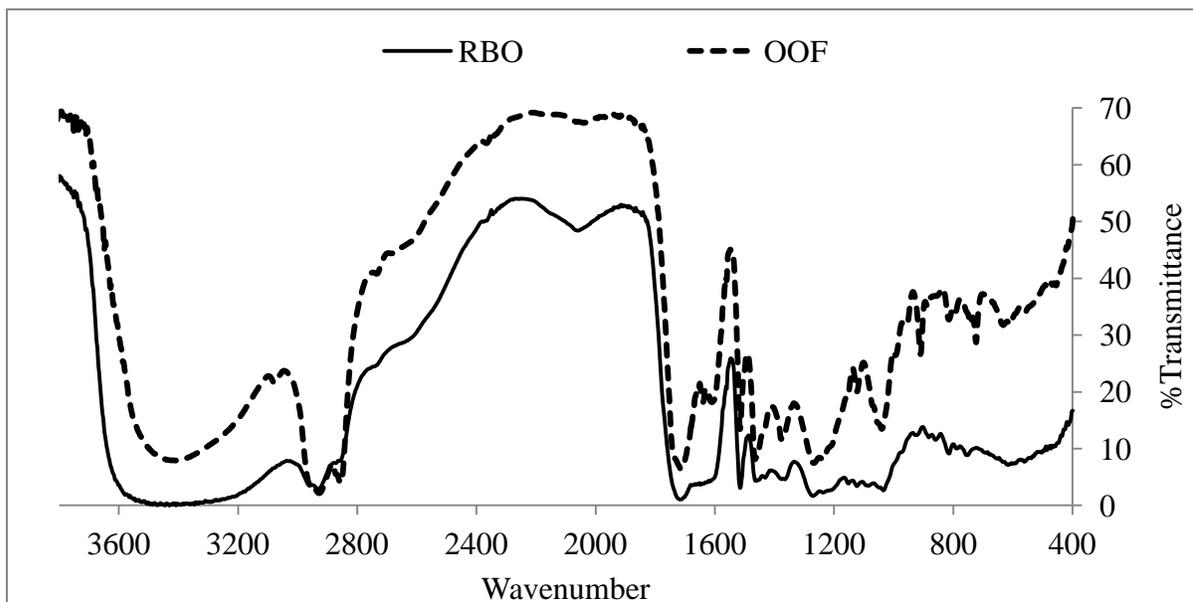


Figure 5. Comparison of RBO and OOF produced from BtOH+OtOH as a solvent treatment samples FTIR spectra.

IV. CONCLUSIONS

The boiler fuel produced from our method had HHV of 34.8 MJ/Kg which is higher than the boiler fuels produced by previous researchers. All three treatments produced high-energy boiler fuel with improved fuel characteristics. However, the combined BtOH+OtOH as an alcohol solvent treatment produced an OOF with higher yield of 56.6% that was, respectively, 13.3% and 6.5% higher than the yields for the BtOH and OtOH treatments alone. The highest reduction of AV for the RBO was also achieved by the BtOH+OtOH mixture treatment. The BtOH+OtOH mixture treatment had an AV of 23.3 mg KOH/g compared to the 92.4 mg KOH/g AV of RBO, a reduction of 74.8%. The HHV of the OOF produced by the BtOH+OtOH treatment was more than doubled to 34.8 MJ/Kg from 16.0 MJ/Kg for RBO, an increase of 117.5%. As compared to RBO the OOF obtained from the BtOH+OtOH treatment water content was reduced by 87.3%; the oxygen content of OOF from the combined alcohol treatment was reduced by 64.3%. From a GC-MS comparison between the RBO and the best OOF produced by this method it was observed that the reduction of acid content was 66.9 area% and the increase of esters and ethers was 120.7 area%.

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