Biodiesel Production from Wild Mustard (Brassica Juncea L.) Seed Oil through Co-Solvent Method at Room Temperature

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Abstract: ***Synthesis of biodiesel from a non-edible feedstcok, namely wild mustard seed oil was the essential target of this work. After oil extraction from the seeds with a yield of 34.0 wt.%, co-solvent alcoholysis of the oil with ethanol and mixed methanol/ethanol system at room temperature (32°C) was studied. Production of biodiesel from the said oil was accomplished via optimized protocol through investigating parameters affecting the biodiesel yield, such as the type of co-solvent, KOH concentration, molar ratio of alcohol/oil, volume ratio of co-solvent/alcohol and reaction period. Maximum ethylic and mixed methyl/ethyl esters yields were obtained under the optimal reaction conditions, and were foubd to be 93.44 and 95.12 wt.%,respectively. The 1HNMR spectroscopy measurements confirmed the conversion of the oil into biodiesels. Besides, fuel properties offered by the fuels obeyed those fixed by ASTM D6751 standard.***

Index Terms: ***Random subspace, REP-tree, Racism, Life expectancy, Random subspaces***

I. INTRODUCTION

Biodiesel (BD) production from edible vegetable oils is controversial as it results in food vurse fuel dispute. As a result, production of BD from non-edible feedstcks is recommnded and was given more concern (Silitonga et al.,2015). As a result of its high erucic acid content, wild mustard plant which originates to Brassicaceae family was regarded a non-edible feedstcok and thus it is not suitable for human consumption. As a result of the high oil content of its seeds, this plant could be used as a potential precorsur for producing BD (Jham et al., 2009).

Co-solvent transesterification was proposed as a means to lessen the heterogeneity between the oil and alcohol, and thus to increase the mass resistance among the reactants molecules, leading to better and faster reaction rate. Different co-solvent were utilized in this aspect, like acetone, ether, Tetrahydrofurane and hexane (Fadhil et al.,2015; Mohammed-Dabo et al.,2012; Alhassan et al.,2014). However, no literature were published on co-solvent alcoholysis of wild mustard seed oil at room temperature to the best of authors knowledge. Synthesis of bidiesels from wild mustard seed oil by co-solvent alcoholysis reaction at room temperature in the presence of co-solvent was the essential goal of this research work. Optimization of the process variables was involved. 1H NMR spectroscopy was applied to affirm the conversion of the oil to the said alkyl esters. Measurment of fuel properties of the resulting biodiesels els were measured as well.

a. Materials and Methods

Seeds of wild mustard were taken from the fields located in the city of Mosul, Nineveh Governorate, north of Iraq during the summer of 2018. After drying the seeds under sun-light for 48h, the dried seeds were ground and then the fed to Soxhlet apparatus for oil extraction using petroleum ether (60-80 °C) for 10h. The oil yield was calculated after solvent stripping from the oil by vacuum distillaltion on a rotary evaporator. Solvents and chemicals utilized in this study were of analytical reagent grade, and were utilized in the production of biodiesels as recieved.

II. TRANSESTERIFICATION OF WMSO IN THE PRESENCE OF CO-SOLVENT

Transesterification reaction assisted by co-solvent was accomplished in a 500 mL three necks round-bottomed flask connected with a condensation system, mechanical stirring, thermostat and sampling outlet. The oil (100g) was fed to the reactor, and then the wanted amount of the co-solvent (petroleum ether (60-80 °C) was added with continuous stirring. Afterwards, KOH in an alcohol solution was freshly prepared and added to the reactor containing the oil-co-solvent mixture. The reaction was then accomplished at the desired temperature for a specified time with continuous stirring. After the reaction was accomplished, glycerin layer was stripped and the alkyl ester layer was subjected to vacuum distillation for removal of both unreacted alcohol and the co-solvent (Fadhil et al.,2015b). The alkyl ester layer was then washed by warm distillated water and dried over sodium sulfate. The BD yield was quantified as follows (Fadhil,2013):

$$\text{Yield of BD}\,(\%) = \frac{\text{Weight of the purified BD}}{\text{Weight of the oil taken (g)}} \text{ X } 100$$

III. BIODIESELS ANALYSIS

The ester content on the prepared BD, was determined by applying procedure suggested by Bindhu et al.(2012). Properties of the as-prepared biodiesels were specified following ASTM standard test methods. The soaps content on the biodiesels was specified by AOCS Cc 17-95, while

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he total glycerin was specified based on method suggested by Pisarello et al.(2010). Triplicate measurement of each property was performed and the obtained date were given as the average ± standard deviation (SD). Conversion of the WMSO to alkyl esters was affirmed by 1H NMR spectroscopy on GmbH 400.22 Mhz. Samples (approximately 150 µL) were diluted in 500 µL of deuterated chloroform (CDCl3) followed by measuring the spectra of samples.

IV. RESULTS AND DISCUSSION

4.1. Feedstcok Properties

The oil content of the wild mustard seeds was ~ 34.0 wt.% which is higher much higher than the oil content of Yucca aloifolia seeds (16.23 wt.%) (Nehdi et al.,2015) and Kapok seeds (22.0 wt.%)(Rashid et al.,2014). The density, kinematic viscosity, flash point, acid value, saponification value and the iodine value of WMSO were, 0.9118,24.13,145°C,2.56 mg KOH/g,190 mg KOH/g and 106.20 mg I2/100 oil, respectively. The WMSO possesses higher level of the unsaturated fatty acids (89.90%) than saturated fatty acids (5.78%). In addition, WMSO consists mainly of erucic acid (45.39%), linoleic acid (11.61%) and linolenic acid (11.45%). It was also noticed that level of mono unsaturated fatty acids in WMSO (67.45%) was higher than that of poly unsaturated fatty acids level (22.45%). Based on work published by Lin and Li,2009, the lower the poly unsaturated fatty acids content oils, the higher the resistance to deterioration in their oxidation stability.

4.2. Co-Solvent Transesterification of WMSO

Suitable transesterification method that must be applied for synthesis of BD is determined by the acid value of its parent oil. Oils with free fatty acids limit of (3-5%) are suitable to produce BD via direct base-catalyzed transesterification (Meher et al.,2006). The WMSO had an aicd value of 2.56 mg KOH/g (1.28 % free fatty acid content) which is below the safe limits for base-catalyzed transesterification and below the acid values of Croton megalocarpus oil and Okra seed oil which were directly used for BD synthesis via base-catalyzed transesterification as well (Kafuku and Mbarawa,2010 ;Anwar et al.,2010). Therefore, synthesis of alkyl esters from the WMSO was accomplished via transesterification reaction with ethanol and mixed methanol/ethanol assisted by a co-solvent (petroelum ether).

Effect of KOH amount on the BD yield was investigated by testing various weight percentages(0.20-1.40 wt.% of oil) while other factors were set fixed at 6:1 alcohol/oil molar ratio, 1:1 alcohol/co-solvent % v/v,60 minutes reeaction time and 60 rpm rate of stirring. As depicted in (Fig.1a), the BD yield incresed with increasing the KOH concentration. However, transesterifcation with etahnol gave the highest BD yield at 1.20 wt.% KOH compared to1.0 wt.% KOH for maximum yield of mixed methyl/ethyl esters. This result attributes to the KOH solubility in the employed alcohol (Fadhil and Ahmed,2018). KOH concentrtions gretaer than the optimal reduced the BD yield due to saponification reaction (Al-Tikrity et al.,2016).

Various alcohol/ co-solvent ratios (0.5:1- 2.5:1 co-solvent/alcohol % v/v) were tested. In all experiments, KOH concentrations was fixed at thier optimal values with fixing speed of stirring, molar ratio of alcohol/oil, and the reaction period at 600 rpm, 6:1, 60 minutes, respectively. It is obvious from (Fig.2b) that th increae of amount of the co-solvent has produced higher yields of biodiesels becasue increasing amount of co-solvent will lessen the oil viscosity as a consequence of the thinning, giving rise to an additional mass transition between the two liquids. The ratio 1:1% v/v mixed methanol/ethanol/co-solvent has produced maximum BD yield, whereas 1:1.5 ethanol:co-solvent was the optimal ratio which gave the highest ethyl esters yiled. However, co-solvent amounts over the optimal minimized the BD yield becasue of the dilution effect on the reactants(Alhassan et al.,2014).

Alcoholysis reaction of WMSO was also conducted using different molar ratio of an alcohol/oil. In all trials, KOH concentrations and alcohol:co-solvent ratios were fixed at thier optmal values as obtained in the previous sections, whilst the rate of stirring and the reaction period were established at 600 rpm and 60 minutes, respectively. A positive increase in the BD yield was observed upon increasing the molar ratio of alcohol/oil molar as depicted in (Fig.2c). Nonetheless, yield of mixed methyl/ethyl estewas attained at 6:1 alcohol to oil molar ratio, while maximum yield of the ethyl esters yiled was obtained at 8:1 ethanol/oil molar ratio. This variance in the alkyl esters yield may be scribed to the solubility of the oil in the alcohol involved which is better in mixed methanol/ethanol system than ethanol, making the mass transfer between the oil phase and alcohol phase better. Nevertheless, molar ratio of alcohol/oil beyond the optimal resulted in lower BD yields due to the hardness of the separation of the two phases because of the soaps formation bringing to lower yield of BD (Aldobouni et al.,2016).

Influence of the reaction time on the BD yield was studied by performing alcoholysis reactions at variant time periods (15-120 minutes). In all trials, other parameters were set at their optimum values except the stirring speed which was fixed at 600 rpm. Fig.1d depicts that upon increasing the reaction time, the BD yiled increased and reached maximum at 60 minutes in the case of mixed methanol/ethanol systme and 75 minutes for ethyl estrs yiled. Durations longer than the optimal could result in in a decrease in the BD yield as a consequence of he oil hydolysis into corresponding free fatty acids (Fadhil and Mohammed,2018).

Variant stirring speed (300 - 900 rpm) were tried on co-solvent alcoholysis of WMSO in order to disclose the optimal stirring rate with establishing other factors at their optimal values. It was observed that lower BD yield was obtained at the lower stirring speed (300 rpm) as displayed in (Fig.1e). Upon the increment of the stirring speed, the BD yield increased.This outcome cold be ascribed to the fact that consistency of the reaction mixture could be improved by raising the stirring speed, making mass transfer among

the reactants better. Thus, the conversion will be enhanced. A stirring rate of 600 rpm was enough to yield maximum conversion of the oil to its biodiesels. Nevertheless, as the stirring speed incresed over the optimal, yields of biodiesels dropped because of the formation of more soaps as a result of reverse act of alcoholysis reaction (Kafuku and Mbarawa,2010b).

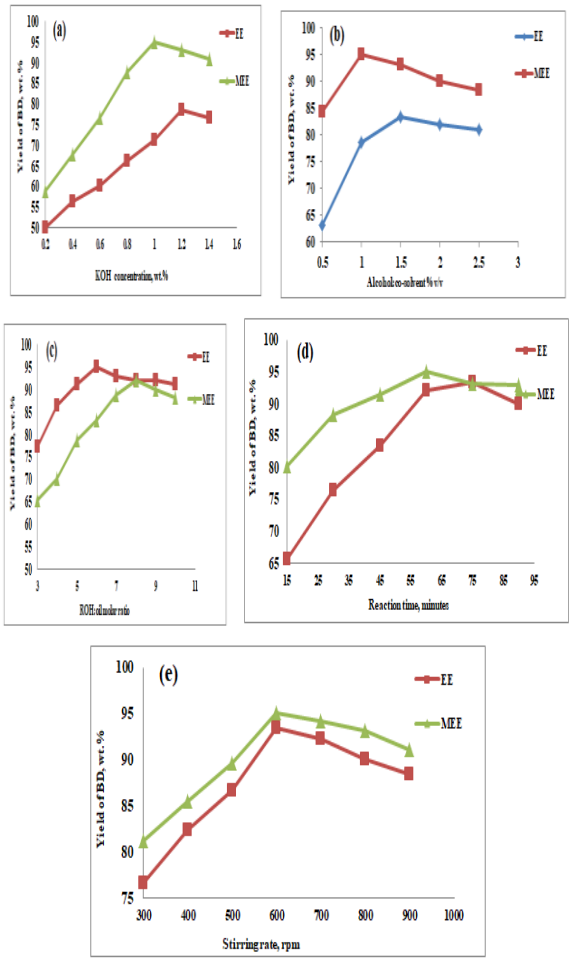

Figure 1. Effect of (a)KOH amount, (b) alcohol/co-solvent % v/v,(c) alcohol/oil molar ratio (d) reaction time, and (e) rate of stirring on BD yield.

Assessment of biodiesels and (biodiesel+petro diesel) blends

The WMSO ethyl and mixed methyl/ethyl esters produced by co-solvent alcoholysis process under optimal reaction conditions were evaluated for thier fuel properties as per ASTM standard test methods in order to assess thier suitibility as fuels for diesel engines, and the results were tabulated in Table 2 which also lists properties of the blends prepared by blending the produced biodiesels with petro diesel (PD) at various volume percentages. The results thus disclosed that proerties of the the parent oil have been positively changed as a result of transesterification with various alcohols. Additionally, the fuel properties of the as-prepared biodiesels met the required limits prescribed by ASTM standards. As seen from Table 1, properties of mixed methyl/ethyl esters were superior to those of the ethyl esters as a consequence of the higher conversion and ester content of the mixed methyl/ethyl esters than the ethyl esters. It is apparent from Table 1 that the kinematic viscosity, flash point, density, and pour point values of PD have been increased with the increment of BD percentage in the prepared blends. These findings could be ascribd to the higher molecular mass of BD than that of PD. However, values of the assessed properties remained within the limits given by ASTM D7467 standards. In contrast, the acid value of PD dropped with the increment of BD level in the prepared blends (Fadhil and Ali,2013). As such, it is possible to use biodiesels from WMSO as fuels for diesel engines and/or they can be successfully mixed with PD.

Table 2. Physical an chemcal properties of biodiesels from WMSO and thier blends with petrod diesel.

Property	*ASTM D6751*	*Ethylic esters*	*Mixed methyl/ethyl esters*
Content of ester,% w/w	-	95.76±1.5	96.88±2.0
Density @ 15.6°C,g/mL	0.9000	0.8891±0.0011	0.8882±0.0011
Kinematic Viscosity @ 40 °C,mm^2/sec	5.0	4.98±0.15	4.58±0.11
Flash Point, °C	130	105 ±1.0	100±1.0
Acid Value, mg KOH / g oil	0.50	0.48±0.02	0.44±0.02
Pour Point, °C	-	-9.0±0.50	-12.0 ±0.50
Refractive Index @20°C	-	1.4508±0.0002	1.4502±0.0001
Total glycerol, wt. %	0.24	0.14 ±0.01	0.11±0.01
Soap, ppm	5.0	1.88±0.15	1.42±0.11
Water content (%)	-	< 0.01	< 0.01

Physico-chemical properties of (BD+PD) blends					
Property	**Density @ 15.6 °C, g/ml**	**Kin. Viscosity @40°C mm^2/s**	**Flash point, °C**	**Acid value, mg KOH/g**	**Pour point, °C**
PD	0.8300	2.67	77	0.45	-16
ME BD	0.8891	4.98	105	0.48	-9.0
B_{10}	0.8433	2.98	82	0.42	-15
B_{20}	0.8543	3.76	85	0.38	-14
B_{30}	0.8551	4.03	89	0.34	-13
B_{40}	0.8599	4.32	93	0.30	-12
B_{50}	0.8695	4.75	98	0.27	-11
MEE BD	0.8882	4.58	100	0.44	-12.0
B_{10}	0.8418	2.97	81	0.38	-15
B_{20}	0.8533	3.73	82	0.34	-14
B_{30}	0.8549	4.0	86	0.32	-13
B_{40}	0.8598	4.22	92	0.29	-12
B_{50}	0.8694	4.55	96	0.26	-12

i) Analysis of biodiesel

Monitoring alcoholysis reaction as well as quantifying the oil conversion into its alkyl esters could be achieved by

using 1H NMR spectroscopy (Ullah et al.,2015). Accordingly, the prepared ethyl and mixed methyl/ethyl esters were analyzed using 1HNMR spectroscopy as depicted in Fig.2. The characteristic peak at 4.11 ppm which acould be assigned to the ethoxyl group of the produced BD and a triplet peak at 2.26 ppm which was ascribed to α-CH2 protons affirm the conversion of WMSO to its ethyl esters (Al-Tikriti et al.,2016). The conversion of WMSO into mixed metyl/ethyl esters was also verified through the presence of both the methy and ethyl groups as can be seen in Fig.2. The detection of α-methylene protons (α-CH2) at 2.01–2.75 ppm as a triplet peak, the methoxy ester protons (-O-CH3) as a strong singlet at 3.7 ppm and a quartet at 4.01–4.02 ppm which assigned to methylenic protons in the ethoxylated group (-O-CH2-CH3) verified the conversion of WMSO into mixed methylic/ethylic esters. The acquired findings imply the merits of alcoholysis reaction on changing WMSO to into a more valuable proucts.

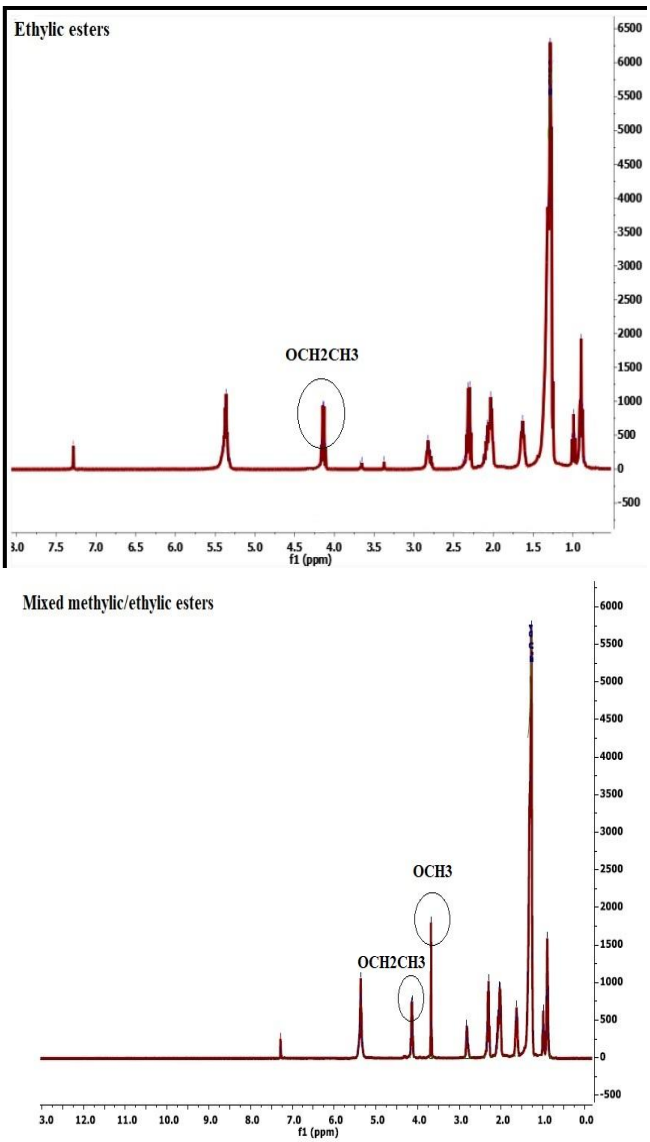

Figure 2. ^{1}H NMR spectra of the ethylic and mixed methylic/ethylic esters form WMSO.

V. CONCLUSIONS

Co-solvent assisted alkali-catalyzed transesterification of WMSO with ethanol and mixed methanol/ethanol at room temperature was successful on converting WMSO to more precious fuels whose properties coincide with limits imposed by ASTM D 6751. Besides, the fuel properties of the blends prepared by mixing the obtained biodiesels with petro diesel at variant percentages were also coincide with those given by ASTM D7467-17 standards. The 1H NMR spectroscopy confirmed the conversion of WMSO into the said fuels.

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