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SHORT COMMUNICATION

Production of biodiesel from non-edible seed oil of *Citrus x aurantium* L.

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Abstract

Majority of the oil seed plants are reported as not fully utilized for economic benefits of the mankind due to lack of technological know-how, and as a result they are thrown out to the environment as organic waste. In the present study, *Citrus x aurantium* L. (Rutaceae), popularly known as Mandarin Orange cultivated in North East India have been used for extraction of oil from its dried seeds and the physiochemical properties of the biodiesel obtained from seed oil were investigated. The experiment with Orange oil for synthesis in a 2 L capacity reactor reveals that a single step transesterification is enough to produce Orange alkyl ester. Molar ratio 1:09 and Catalyst 1.5 wt% were found to be optimal. Other parameters such as reaction temperature at 65 °C, time 120 minutes and speed 500 rpm resulted into 94% oil yield. It is our suggestion to explore the large-scale production of Mandarin Orange seed oil-based biodiesel, which will promote our sustainable energy goals. It was found that the scope is immense given the consumption of Orange and the oil content of the seeds.

Keywords: *Citrus x aurantium*; Mandarin Orange; Orange Seed Oil; Biodiesel; Energy; Fuel; Diesel Engine

1. Introduction

From the inception of civilization, human kind has invested time and resources to preserve biodiversity and experienced the benefits it offers in terms of food, energy and shelter. Biodiversity of India is vast which paves the way for nurturing various plants and oil-bearing seeds. Various oil-bearing seeds which are not popular as food have been investigated by several researchers throughout the world as supplementary diesel engine fuel to power diesel engine (Azam et al., 2005; Demirbas, 2007; Chavan et al., 2014; Demirbas et al., 2016; Dash and Lingfa, 2017). The energy security is the need of the hour considering the worldwide state of affairs. Pioneering works have been accomplished by many researchers in this area (Agarwal, 2007; Lingfa, 2013; Dash et al., 2018). Many oil-bearing seeds have been experimented in the compression ignition engine by using the oil expelled from the seeds. Due to the cost criterion, edible seeds are not encouraged, albeit many works are also available which uses biofuel prepared from edible oil as diesel engine fuel (Fangrui and Hanna, 1999; Fukuda et al., 2001; Murugesan et al., 2009; Mofijur et al., 2013). Many benefits have also been reported for biofuel in general or biodiesel in particular such as equivalent diesel performance, lesser emissions and carbon neutral nature of biodiesel. One among such oil-bearing seed is the Orange seed. Orange is very famous fruit crop cultivated in India and China throughout the year and it is consumed as food and nutraceutical agent. It is reported to be used for largescale production of juice as dietary routine due to its rich Vitamin C and other important nutrient content and also reported to be offered in temples for *Prasada* making. A typical orange contains 12 carpels and 15-20 seeds for a matured orange. Usually, the orange seeds are thrown away after extracting the juices. Traditionally, orange seed oil has been used for skin moisturizer as it has smoothening and revitalizing effects. Usually, the cold press methods are used to extract the oil from the seeds. Biodiesel is usually produced from the seed oil by reacting it against an alcohol (Meher et al., 2006; Moser, 2011; Leung et al., 2010; Abbaszaadeh et al., 2012). The biodiesel prospects of Orange seed oil is reported to be promising due to availability of the raw materials (Rashid et al., 2013; Azad, 2017). Detail production process and yield optimization has been carried out in present studies. However, before proceeding to the transesterification process, the acid value needs to be checked. If the acid value is more than 5 mg KOH/g, then a pre-treatment process has to be followed to reduce the free fatty acid content (Marchetti et al., 2007; Patil and Deng, 2009; Shahid and Jamal, 2011; Santacesaria et al., 2012). The pre-treatment is an acid treatment step where the FFA is reduced to desired limit.

2. Materials and methods

The Orange fruit has been collected from the local vendor sitting along the road side market of Nirjuli, Arunachal Pradesh (latitude 27.13°N and longitude 93.74°E) in the month of December 2021 (Figure 1A). The seeds were extracted and dried in open sun light for 3 days to remove moisture content. The dried seeds were expelled in a local mechanical oil expeller to extract seed oil. Almost 31 wt% oil content were obtained from the expelled seeds (Figure 1B). The acid value was estimated and found to be 2.53 mg KOH/g for the filtered oil. Hence, the acid pre-treatment was not sought for the biodiesel synthesis. The required chemicals and reagents such as methanol, sulphuric acid, NaOH and isopropyl alcohol were purchased from Merck Pvt Ltd. The biodiesel was prepared in biodiesel laboratory, Department of Mechanical Engineering, NERIST, Nirjuli, Arunachal Pradesh. Transesterification was processed in the 2L capacity reactor as shown in Figure 1C. The reactor shown in the Figure 1C essentially consists of heater with mechanical stirrer. The Orange oil to methanol molar ratio, catalyst amount (NaOH), temperature, time and rpm were optimized in this study. The fuel properties were evaluated as per standard ASTM methods. As the raw oil was not investigated for engine trial, the physical and chemical properties of the raw Orange oil were not done except for the acid value. The cetane number of the fuel sample was measured as per ASTM D613. The acid value of the fuel sample was measured as per ASTM D664 method. The kinematic viscosity was also measured as per ASTM D445 method. The density of the fuel sample was measured as per ASTM D1298. The calorific value of the test sample was also measured conforming to ASTM D4809 method. The flash point of the test sample is measured confirming to ASTM D93. The pour point of the fuel sample was measured as per ASTM D97 method.

3. Results

3.1. Effect of molar ratio and catalyst amount on biodiesel yield

Molar ratio of oil to methanol varied from 1:03 to 1:15 for various NaOH amount (0.5 wt% to 2.5 wt%). The results of molar ratio and catalyst NaOH amount on biodiesel yield (%) is presented in Table

1. At a molar ratio of 1:03, for catalyst amount 0.5, 1, 1.5, 2 and 2.5 wt%, the biodiesel yields were observed to be 46%, 58%, 77%, 72% and 64% respectively. At a molar ratio of 1:06, for catalyst amount 0.5, 1, 1.5, 2 and 2.5 wt%, the biodiesel yields were observed to be 61%, 74%, 88%, 81% and 677% respectively. At a molar ratio of 1:09, for catalyst amount 0.5, 1, 1.5, 2 and 2.5 wt%, the biodiesel yields were observed to be 62%, 78%, 93%, 87% and 81% respectively. At a molar ratio of 1:12, for catalyst amount 0.5, 1, 1.5, 2 and 2.5 wt%, the biodiesel yields were found to be 53%, 69%, 86%, 81% and 71% respectively. At a molar ratio of 1:15, for catalyst amount 0.5, 1, 1.5, 2 and 2.5 wt%, the biodiesel yields were found to be 41%, 51%, 76%, 67% and 55% respectively.

3.2. Effect of reaction temperature on biodiesel yield

The results of reaction temperature on biodiesel yield (%) is presented in Table 2. The reaction temperature was found to be varied from 45 °C to 70 °C at the interval of 5 °C. At reaction temperature of 45 °C, 50 °C, 55 °C, 60 °C, 65 °C and 70 °C the biodiesel yield (%) was found to be 55%, 68%, 82 %, 93%, 94% and 80% respectively.

3.3. Effect of reaction time on biodiesel yield

The results of reaction time on biodiesel yield (%) is presented in Table 3. The reaction time was recorded from 20 minutes to 160 minutes in the interval of 20 minutes for biodiesel yield (%). At reaction time of 20, 40, 60, 80, 100, 120, 140 and 160 minutes, the biodiesel yield (%) was found to be 45%, 61%, 73%, 84%, 92%, 94%, 94% and 93% respectively.

3.4. Effect of reaction speed on biodiesel yield

The results of reaction speed on biodiesel yield (%) is presented in Table 4. The reaction speed was recorded to be varied from 300 rpm to 700 rpm at the interval of 100 rpm. At reaction speed of 300, 400, 500, 600 and 700 rpm the biodiesel yield (%) was recorded to be 67, 86, 94, 94 and 94% respectively.

3.5. Fuel sample properties

Main properties of prepared biodiesel have been measured in the present studies are presented in Table 5. The acid value of biodiesel was found to be 0.17 mg KOH/g. The kinematic viscosity was recorded to be 3.89 cSt@40°C for the biodiesel sample, whereas it is reported to be 2.7 cSt@40°C for the diesel fuel. The density of the prepared biodiesel obtained was recorded to be 0.874 gm/cc, whereas it is reported to be 0.830 gm/cc for the standard diesel. The calorific value of Orange biodiesel obtained was recorded to be 38245 kJ/kg, whereas it is reported to be 42500 kJ/kg for the diesel. The cetane number of the prepared orange biodiesel was recorded to be 51, whereas it is reported to be 48 for the diesel fuel. The flash point of the biodiesel was recorded to be 188°C, whereas it is reported to be 65°C for the diesel fuel. The pour point of the Orange biodiesel was recorded to be 2.5 °C, whereas it is reported to be -8.6 °C for the baseline diesel fuel.

Figure 1A. The fresh and ripen Orange (*Citrus x aurantium* L.) fruits collected from local vendors for extraction of seed oil; 1B. The sun dried Orange seeds from ripen orange used as raw material for non-edible biodiesel production; 1C. Biodiesel reactor used for extraction of orange seed oil for biodiesel processing.

Table 1. Effect of molar ratio and catalyst amount on biodiesel yield (%)

Molar ratio (Orange oil to Methanol)	0.50wt%	1.00wt%	1.50wt%	2.00wt%	2.50wt%
1:03	46	58	77	72	64
1:06	61	74	88	81	77
1:09	62	78	93	87	81
1:12	53	69	86	81	71
1:15	41	51	76	67	55

Table 2. Effect of reaction temperature on biodiesel yield

Reaction temperature (°C)	Biodiesel yield (%)
45	55
50	68
55	82
60	93
65	94
70	80

Table 3. Effect of reaction time on biodiesel yield

Reaction time (Minutes)	Biodiesel yield (%)
20	45
40	61
60	73
80	84
100	92
120	94
140	93
160	93

Table 4. Effect of reaction speed on biodiesel yield

Stirring speed (rpm)	Biodiesel yield (%)
300	67
400	86
500	94
600	94
700	94

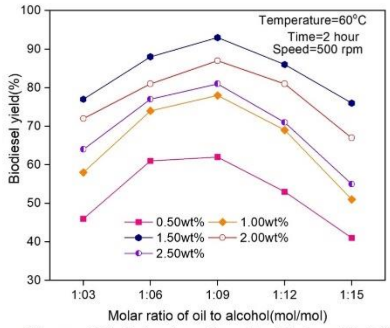

Figure 4. Effect of molar ratio and catalyst on BD yield

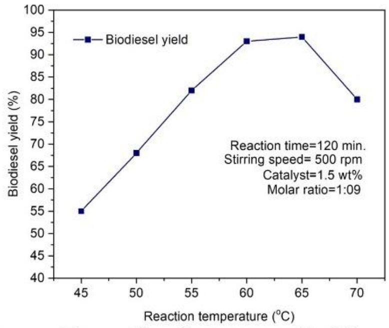

Figure 5. Effect of temperature on BD yield

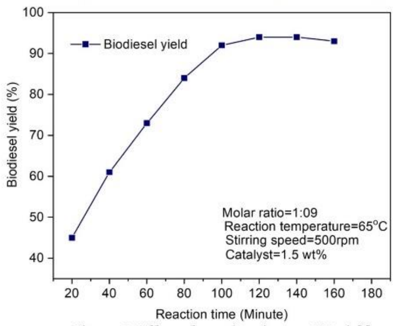

Figure 6. Effect of reaction time on BD yield

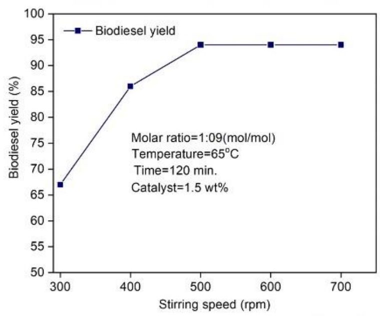

Figure 7. Effect of stirring speed on BD yield; BD=Biodiesel

4. Discussion

In the present studies, the acid value of the Orange seed oil was found to be 2.53 mg KOH/g while the FFA value was reported to be 1.27%. The FFA was found well below the pre-treatment deciding FFA value of 2.5%. The oil sample was taken for transesterification process where the alcohol and triglyceride reacted to get the biodiesel and glycerol in the presence of a catalyst. Triglyceride is basically any plant-based seed oil. Methanol or ethanol are usually used as alcohol for biodiesel production (Sharma et al., 2008; Verma and Sharma, 2016). Apart from methanol, Sodium hydroxide (NaOH) is also used as catalyst to speed up the synthesis of the chemical reaction. The biodiesel is fundamentally a methyl or ethyl ester.

Methanol was used as catalyst in the present study. The correct proportion of methanol and NaOH is desired (Chavan et al., 2014). Both the parameters have been optimized in present study. The molar ratio of methanol and NaOH when increased was found to enhanced biofuel conversion. The increase in NaOH quantity also favours the synthesis. However, the optimum value for NaOH was found to be 1.5 wt% and the optimal molar ratio at which the biodiesel yield was found to be 93% which is 1:09 (Table 1 and Figure 4).

It was also considered to evaluate the optimal condition for time, temperature and speed of synthesis. Initially, 60 °C, 2 hour and 500 rpm fixed before evaluating individual optimum values. The reaction temperature was found greatly enhanced the yield. The chemical synthesis accelerated with increase in temperature. Best yield of 94% was observed at the temperature of 65 °C (Table 2 and Figure 5). Exceeding beyond 65 °C was found to have detrimental effect on yield. This is probably because of the fast evaporation of bulk alcohol from the mixture to the condenser (Van, 2005; Aransiola, 2014).

As far as reaction time is concerned, the originally 2 hour time taken was found to be perfect (Table 3 and Figure 6). In the present study, the initial 60 minutes has resulted into more than 70% biodiesel yield. However, the rate of increment of biodiesel yield decreased with time as a result of further scope of chemical reactivity. In another study, reaction time of 120 minutes were reported to be ideal for optimum biodiesel yield (Shahid and Jamal, 2011).

The stirring speed of 500 rpm was found to be optimal for biodiesel yield (Table 4 and Figure 7). Increasing the stirring speed did not change in yield increment except the consumption of more electricity. Drastic increase of yield (%) by increasing the reaction speed beyond 300 rpm may be ascribed to the fact that the chemical reactivity accelerated with the increasing speed of the reaction mixture (Verma and Sharma, 2016).

The kinematic viscosity of the prepared biodiesel has been observed to be little higher compared to petroleum diesel. This may be due to the long chain length of the biodiesel molecules and high raw oil viscosity. The flash point of biofuel obtained from orange seed oil was found significantly higher when compared with diesel fuel. From the view point of storage safety, the biodiesel is advantageous compared to petroleum diesel. Pour point of the prepared biofuel was observed to be more than diesel pour point. However, a temperature of 2.5 °C is very high keeping in view the average temperature of Indian climate. Other properties of the prepared biodiesel such as acid value, density, calorific value and cetane number also found to be comparable to that of diesel engine. Finally, it is seen that the prepared liquid biofuel obtained from Orange seed oil is of standard quality which conformed to the limits and values of physico-chemical properties of diesel fuel (Table 5) recommended by ASTM.

Table 5. Physico-chemical properties of the fuel sample of Orange Biodiesel compared with Diesel

Property	Orange Biodiesel	Diesel	Methods
Acid value (mg KOH/g)	0.17	—	ASTM D664
Kinematic Viscosity (cSt@40˚C)	3.89	2.7	ASTM D445
Density (gm/cc)	0.874	0.830	ASTM D1298
Calorific value (KJ/kg)	38245	42500	ASTM D4809
Cetane number	51	48	ASTM D613
Flash point (˚C)	188	65	ASTM D93
Pour point (˚C)	2.5	-8.6	ASTM D97

4. Conclusions

In the present studies, the biodiesel produced from Orange Seed oil using 2 L capacity laboratory-based reactor and the Molar ratio 1:09, Catalyst 1.5 wt%, reaction temperature of 65 °C, time 120 minutes and speed 500 rpm has revealed optimum biodiesel yield of 94%. The physicochemical properties of biodiesel have been found to be conformed to the required quality of ASTM standard and the values obtained are also close to the physicochemical properties of diesel fuel. The important key fuel properties such as kinematic viscosity and density was found to be reduced to a safe limit after transesterification process. As biodiesel has been reported as a biodegradable, sustainable and cleaner alternative to petroleum diesel which offer potential environmental and energy benefits, we recommend to produce this in large scale to satisfy the energy need of the current century. Biofuel project will only become successful when diverse feedstocks are studied and exploited. It is recommended to study the application of our prepared biodiesel sample as an outcome of the present studies in the combustion engine for the performance and emission level test. Further study could be extended to analyse the long and short period durability test.

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Author's contribution

Santosh Kumar Dash (SKD): conceptualisation, original draft, writing-reviewing-editing. Pradip Lingfa (pl): writing-reviewing-editing, supervising. Dharmeswar Dash (DD): writing-reviewing-editing.

Conflict of interest

The authors have no conflict of interest.

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