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An Efficient Utilization of Waste Date Pit Oil for Ethyl Ester Production

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As a green material, date pit oil is increasingly utilized as an inexpensive feedstock for ethyl ester (biodiesel) production. Waste date pits as a raw material are one of the highly produced agricultural wastes in Iran. This study investigated the effect of several procedure parameters including the ethanol/oil molar ratio, reaction temperature and amount of catalysts on the yield of the produced ethyl ester. The activity of date pit oil can be considered a method of second-generation biofuels production including green diesel fractions. Efficient from waste date pits and synthesis of ethyl ester have made a breakthrough in biodiesel production. Gas chromatography/mass spectrometry (GC-MS) and Fourier transform infrared (FT-IR) were employed to determine the composition of product. The optimized ethyl ester yield obtained was 92% when the procedure temperature was 65 °C, within 6h, with 7:1 ethanol/oil molar ratio with 0.75 wt.% of catalyst (KOH). Waste date pits oil as feedstock can be an efficient platform for ethyl ester production. The purified ethyl ester satisfies the stringent quality standards imposed by ASTM D-6751 (USA standard) and EN-14214 (European standard).

Keywords: Waste date pits, Ethyl ester, Trans-esterification, Extraction

INTRODUCTION

Efforts have been devoted to reduce the emission and detrimental consequences of industrial sources [1-3] due to increasing climatic problems of greenhouse gas emissions [4-6]. As a way to solve these problems, renewable energies [7,8] like biodiesel which usually refers to ethyl esters is considered a beneficial and environment-friendly alternative biofuel for diesel engines [9]. One method of biodiesel production is trans-esterification reaction with light alcohol, usually methanol and ethanol [10]. Triglycerides as waste oil react with alcohols like ethanol and convert to ethyl ester and glycerine in the presence of suitable catalyst [11,12]. Biodiesel which is a biodegradable, nontoxic fuel burning with a low sulphur and carbon monoxide is environmentally favorable in terms of oil and fat recycling [1,13].

Several factors such as excessive accessibility, the carbon neutral nature of fuels derived from biomaterial, and profusion of resources have supported the value of fuels as an economically potential source which is environmental-friendly [14]. As a subtropical and tropical tree, date palm is mainly grown in arid, warm regions in the Middle East [15]. Iran is the first country in terms of palm cultivation and the second one in palm production. In addition to its nutritional values, palm is a non-oil exporting product of Iran's Southern provinces. So, date pit oil as a non-edible source was considered to be the best potential alternative raw material for ethyl ester production [14]. Date pit which is obtained as a waste material in many food production factories accounts for 10-15% of the total date weight [16]. This huge volume of remnant which brings about environmental problems can be used in biofuel production [17]. In their study, Abu-Jrai *et al.* revealed that the synthesized KOH supported waste date pits carbon catalyst and resulted in high performance by obtaining high biodiesel yield. The optimum FAME yield was 91.6% attained at 65 °C, 9:1 methanol to oil ratio in 60 min [15]. In another paper, Al-Muhtaseb *et al.* showed the synthesis of

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active catalysts from waste date pits carbon produced by carbonization and impregnation with Pt and Pd metals [14]. In this study, date pit was used as a cost-effective primary substance for biodiesel production. In this work, ethyl ester was produced using date pit oil. In order to touch the maximum yield of ethyl ester production, agents including the ethanol/oil molar ratio, concentration of catalyst and reaction temperature were examined. Trans-esterification of waste date pit oil was performed in the presence of KOH as a homogeneous catalyst. The trans-esterification process was done in temperature range of (25-75 °C). Amount of catalyst was used based on waste oil weight (0.25, 0.5, 0.75 and 1 wt.%). Furthermore, ethanol/oil molar ratio was adjusted of (3:1, 5:1, 7:1 and 9:1). Solvent (n-Hexane) should be separated from production; the final ethyl ester should also be alcohol or water free [18].

EXPERIMENTAL

Materials

All the materials used in this study were the chemical reagents of Merck Company (Germany). Waste date pits were obtained from Abas shatter restaurant in Tehran. In the procedure of conducting this work, the following devices were used: heater magnetic stirrers Heidolph (Germany), crushers Model E300 (Italy), rotary evaporator device, STRIKE-ROTAING evaporator model 102.202 (Italy), and FT-IR which was attained using a model 8700 Nicolet Thermo spectrometer in attenuated total reflection. Spectra were recorded with a 4 cm^{-1} resolution and 32 scans at a wave length range of 500-3500 cm^{-1}.

Oil production from Waste Date Pit

First, date pits were washed, dried, and then pulverized by the crusher. Using a paper cotton, the pulverized pits were placed in Soxhlet juice extractor fitted with a 0.5 l round bottom flask. The n-Hexane solvent was boiled and vaporized in the reservoir and converted into fluid after passing the condenser tube. Then, the fluid was poured on the date pit in the Soxhlet extractor. The process was repeated up to the completion of oil extraction from date pit. Finally, the solvent and the oil were separated by rotator in 80 °C and 120 rpm (Fig. 1). After this phase, the oil of waste date pits was analyzed with FT-IR and GC-MS. The results of analyses showed that the produced oil from waste natural materials has the necessary conditions for further use.

Trans-esterification of Date Pit Oil

Using chromatography method, the date pit oil showed 45.45% oleic acid, 20% lauric acid, 4% stearic acid, 8.5% linoleic acid, 11% palmitic, and 12% meristic. In this stage, 20 g of date pit oil with different oil/alcohol ratios was underwent refluxing and mixing with 200 rpm at different concentrations of KOH catalyst in different temperatures for six hours. At the end, the produced biodiesel was separated from glycerine by separating funnel [12]. After course, glycerine and ethyl ester products are separated in 2 phases by decantation (Fig. 2) [19]. To neutralize the produced biodiesel, the product was washed with 60 °C water for three times until the waste water became clear and the biodiesel was weighted. At the end, the two phases of water and ester were separated based on density difference by separating funnel. The ester phase was washed with hot water up to pH neutralization stage and dewatered by sodium sulfate. Finally, the biodiesel yield was calculated according to the following formula [1,20]:

$$\text{Ethyl ester yield (\%)} = (\text{Weight of ethyl ester})/(\text{Weight of waste date pits oil}) \times 100\% \quad (1)$$

The product obtained from trans-esterification is evaluated with fuel quality standards. Also, the obtained ethyl ester is analyzed using FT-IR.

RESULTS AND DISCUSSION

The Effect of Reaction Temperature

The trans-esterification is an endothermic reaction and if the process temperature increases from 25 °C to 65 °C, the ethyl ester yield (Fig. 3) caused when at high temperatures the affinity of carbonyl group in free fatty acid increases towards the nucleophilic ethanol and activation reaches the maxim. Under this circumstance, trans-esterification increases and reaction moves in the forward direction to result in maximum biodiesel yield. However, when the temperature was enhanced further to 65 °C, the ethyl ester

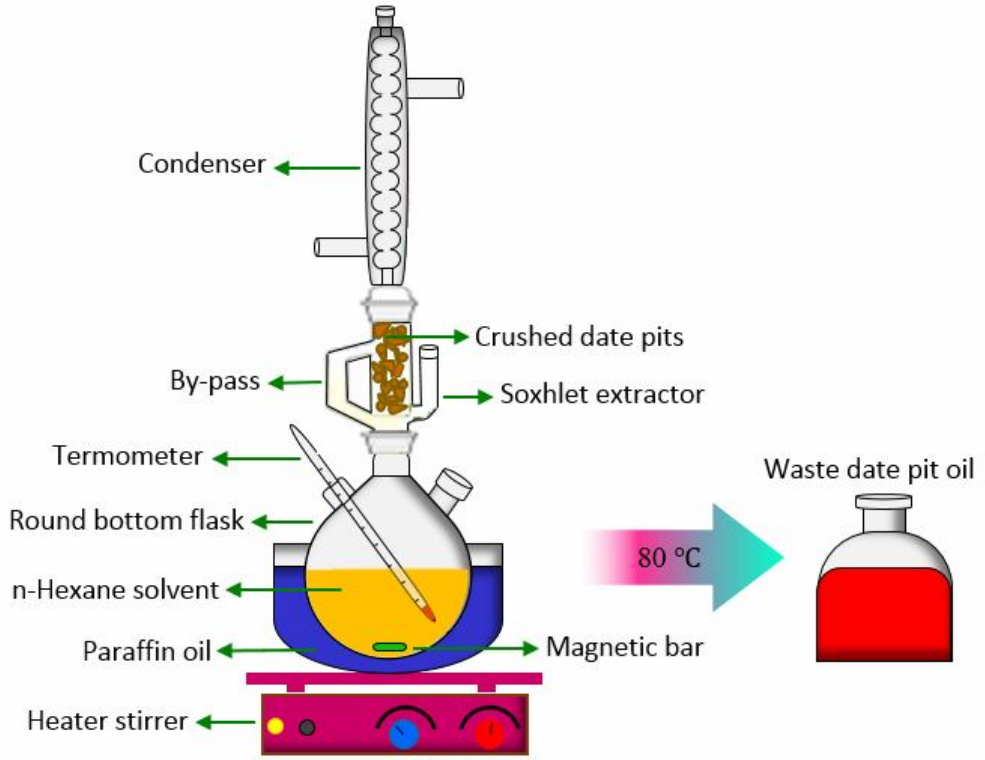

Fig. 1. A schematic of date pit oil extraction.

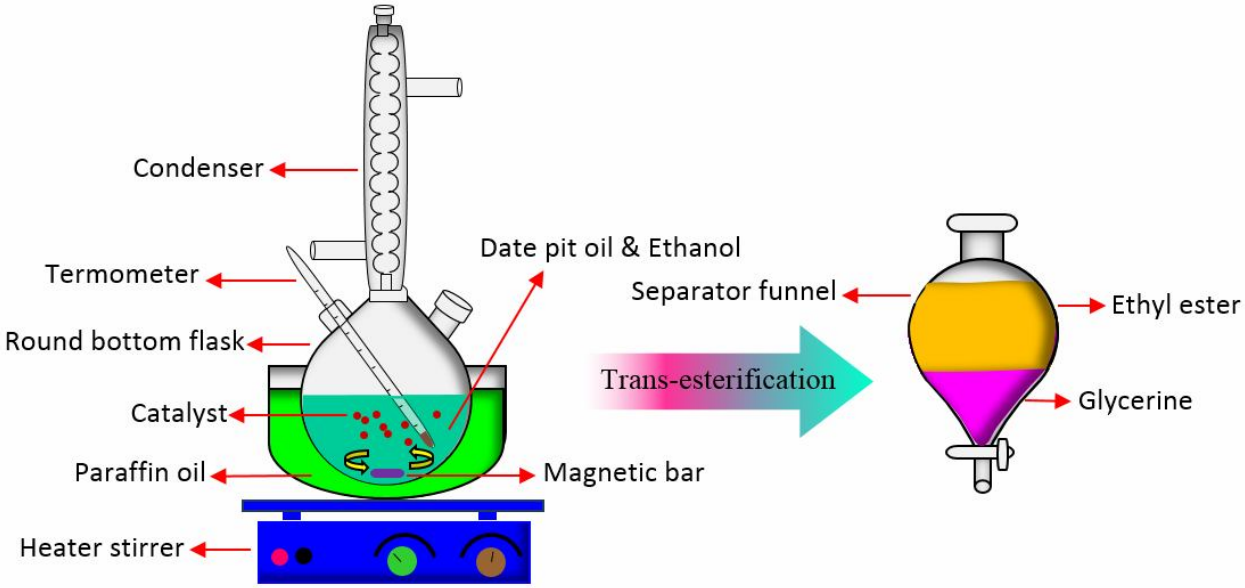

Fig. 2. A schematic of *Trans*-esterification reaction.

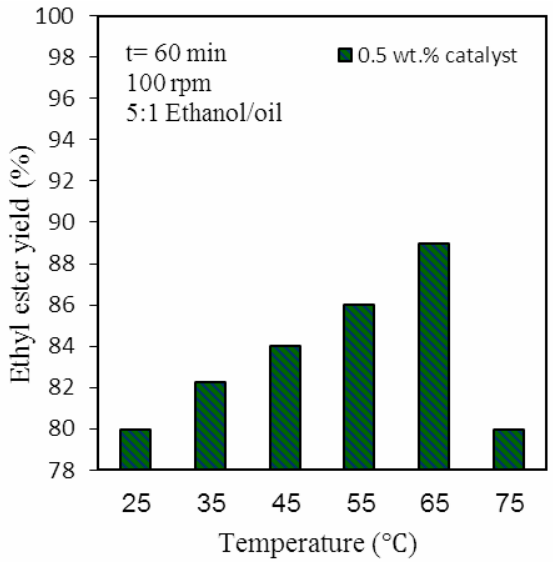

Fig. 3. Effect of temperature on the ethyl ester yield.

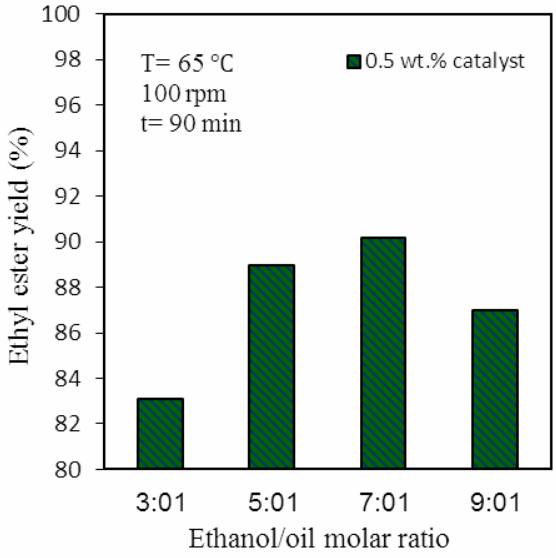

Fig. 4. Effect of ethanol/oil molar ratio on the ethyl ester yield.

yield dropped probably because of the unavailability of the required amount of ethanol for reaction since ethanol evaporation increases and ethyl ester yield decreases with temperature increase. The decrease in ethyl ester yield at higher temperature may be attributed to another variable which is the decrease of ethanol polarity [12,21].

The Effect of Ethanol/Waste Oil Molar Ratio

Figure 4 shows the effect of ethanol/oil ratio on ethyl ester yield which is considered to be an important variable

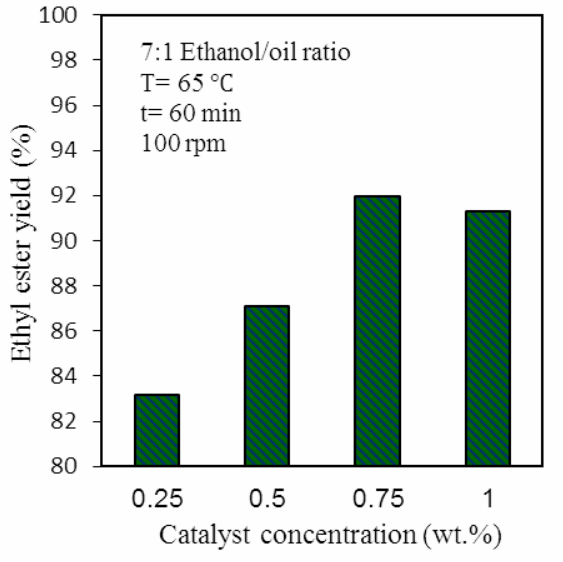

Fig. 5. Effect of catalyst concentration on the ethyl ester yield.

for trans-esterification of waste oil. It is a reversible reaction because the alcohol excessive volume is needed for moving the equilibrium towards the right hand side and oil conversion for maximum ethyl ester yield [1]. Moreover, if the molar ratio enhances, the ethyl ester yield decreases which can be ascribed to the fact that higher molar ratios may hamper the separation of the by-product separation causing difficulties in heating system the reaction mixture. When the alkaline catalyst increases to 0.5 wt.%, the ethyl ester yield reaches 90.2%. This is done because the ethanol/oil molar ratio increases in the mixture of reaction and the active and nucleophile CH_3-CH_2O^- attacks glyceride molecule to form ethyl ester [1,22]. Therefore, suitable ethanol/oil molar ratio results in maximum ethyl ester yield, which was found to be 7:1 in reaction. Generally, it can be said that the highest yield of ethyl ester in the presence of 0.5 wt.% of the catalyst is obtained at 65 °C in 90 min and 100 rpm agitator speed.

The Effect of Catalyst Amount

In trans-esterification reaction, catalyst decomposes ethanol and CH_3-CH_2O^- is produced as a result of this decomposition which is the active species of the reaction. In this reaction, three moles of ethanol are consumed and one mole of ethyl ester is produced. The proper amount of catalyst is necessary for increasing yield of ethyl ester. The excessive increase of catalyst can lead to saponification of the reaction and reduction of the production yield. The most appropriate catalyst was detected to be 0.75 wt.% indicating that the alkaline catalyst with the highest amount of KOH provides more activity compared to 0.5 wt.% of catalyst for reaction to occur with the maximum ethyl ester yield. An increase of KOH more than 1 wt.% causes saponification; so, the optimized amount of concentration was considered 0.75 wt.% (Fig. 5). In order to optimize the catalyst amount, in which the other variables are fixed, the least amount of alkaline catalyst is examined to prevent saponification. In this section, 0.25, 0.5 and 0.75 wt.% amounts were examined respectively. Regarding the saponification of the reaction in 1% of the catalyst molecular weight, 0.75 wt.% was introduced as the optimized amount.

FT-IR Spectrum Results

In this study, after trans-esterification reaction, purification, and separation stages, the FT-IR spectrum of the samples was taken (Fig. 6). All spectrums of triglyceride had a very weak peak in 3470 cm^{-1} which is related to carbonyl ester of triglycerides. A sign near 2960 cm^{-1} and a peak near 3007 cm^{-1} are also observed in all spectrums which are assigned to olefin and *trans* and *cis* dual stretching bonds. The interference of these two peaks is very low but the *trans* peak intensity is lower because the

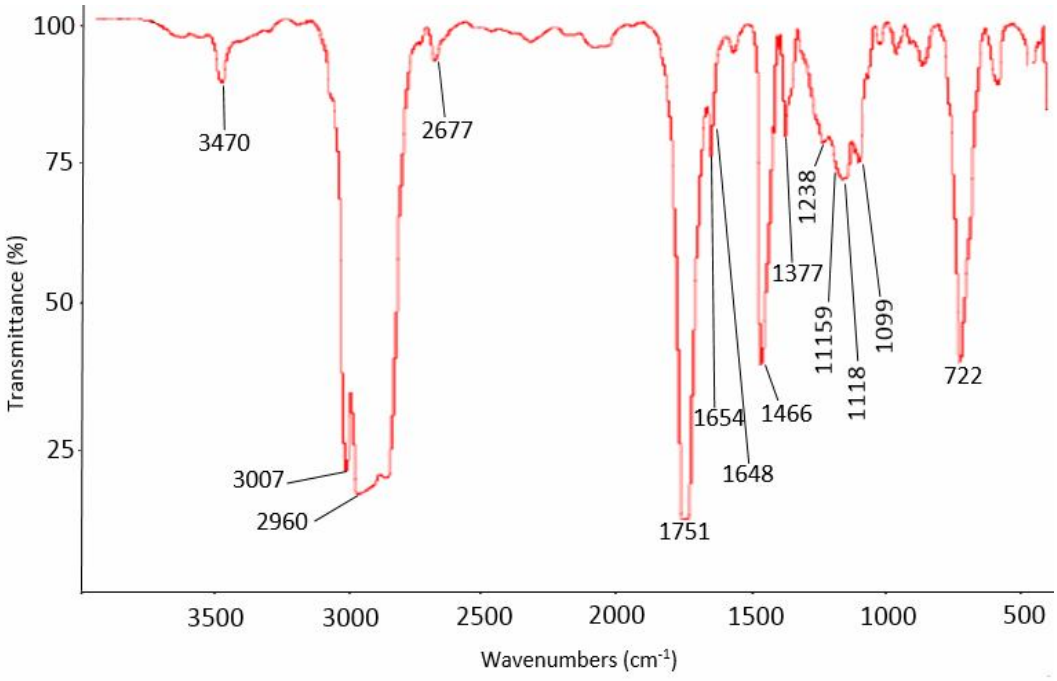

Fig. 6. FT-IR spectra of waste date pit oil.

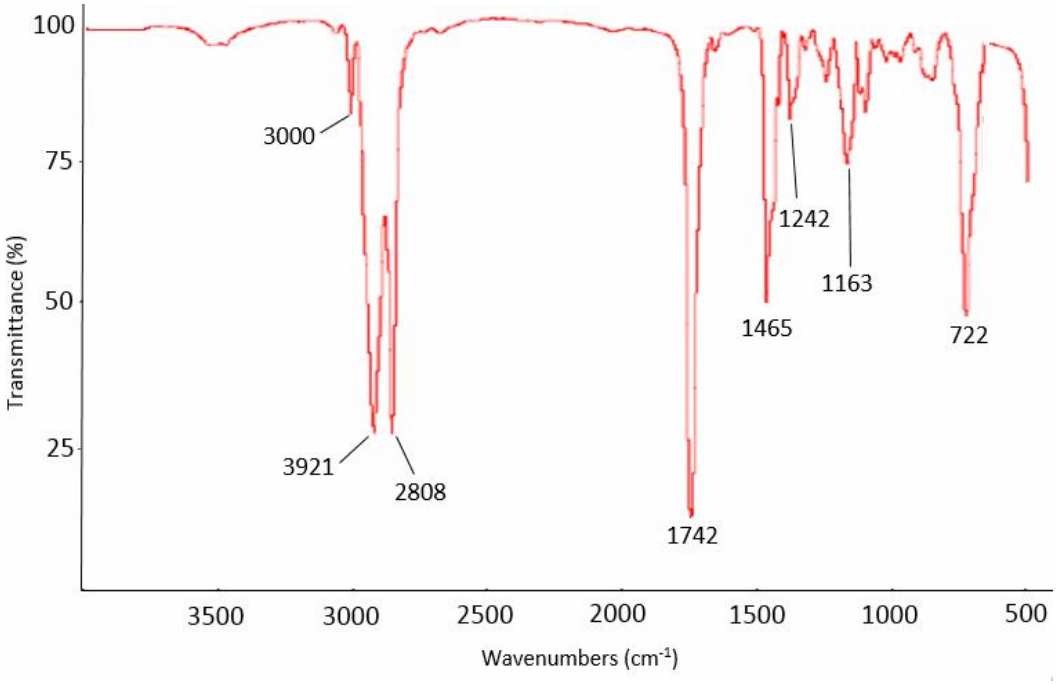

Fig. 7. FT-IR spectra of ethyl ester production.

trans isomer amounts are low in oils. Carbonyl group of waste oil shows a stretching resonance peak at about 1751 cm^{-1}. In all samples, two peaks can be seen in 1654 cm^{-1} and 1648 cm^{-1} and the intensity of the second peak is very subtle in some samples. The small peak is related to -C=C- of unsaturated acyl groups. The peak of 1466 cm^{-1} is the result of bending resonance of $-CH_2$ and CH_3 of aliphatic groups. The ever-present peak at cm in all the samples can be attributed to fluctuating resonance of 1377 cm^{-1} bonds of olefin *cis*. Specification of 1000 to 1400 cm^{-1} area is difficult; however, majority of considerable changes occur in this area. The peak in 1377 cm^{-1} can be attributed to symmetrical bending resonance of ethyl groups. Usually, rocking and scissoring resonance of $-CH_2$ are observed in 1150-1350 cm^{-1} area. Peaks are observed in 1118, 1159, 1238 in 1099 cm^{-1} and shoulder is seen in 1024 cm^{-1} which can be attributed to stretching resonance of C-O groups including two asymmetrical paired resonances of O-C-C and C-C(=O)-O. In some reports, 1238 cm^{-1} peak is attributed to bending resonance out of ethylene group.

Biodiesel FT-IR Spectrum

The FT-IR spectra of ethyl esters are greatly similar to oil spectra except for fingerprint area. The only occurred change in oil structure is glycerol extraction and methanol replacement in hydrocarbon chain. The biggest change is related to 1000 to 1500 cm^{-1} which shows the complete synthesis of biodiesel. The frequency of 1465, 1242 and 1163 cm^{-1} shows functional groups of $-O-CH_3$, $-O-CH_3$ and $-C-O-(CH_3)$ concerning the bending, rocking and stretching motions of symmetric resonance of mid, mid, and high intensity levels, respectively (Fig. 7).

CONCLUSIONS

Date is among the most important products of dry areas and Middle East countries. Date pit oil can be used as a rich source of ethyl ester production. In this study, the date pit oil was extracted by n-Hexane solvent. The highest yield of trans-esterification was obtained (92%) in the presence of KOH catalyst (0.75 wt.%) and 7:1 alcohol/oil molar ratio in 65 °C for 6 h with 200 rpm stirrer. Characterization of physical properties of biodiesel including density was 0.84 g cm^{-3} at 40 °C, flash point was shown to be 167 °C, cloud point and pour point of biodiesel were 0 and -14 °C. Thus, waste date pit oil showed its potential in the biorefinery to produce ethyl ester. Based on the current observations, it can be concluded that waste date pits can be used for many purposes to obtain useful fractions of ethyl ester.

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