The characteristics of peanut and rapeseed including high oil content, favorable fatty acid composition, low agricultural inputs, definable growing season, and uniform seed maturation rates makes them a good source for biodiesel production. Thus, the transesterification process to produce biodiesel from peanut oil and rapeseed oil was studied. This process gives yields of (95% and 88%) from peanut oil and (97%, 92%) from rapeseed oil using potassium hydroxide (KOH) and sodium hydroxide (NaOH) as a catalyst, respectively. Biodiesel yields were analyzed using the FTIR (Fourier Transform Mid-IR) spectroscopy method. Biodiesel yields from peanut oil and rapeseed oil at different conditions were investigated in order to optimize the process. Response surface methodology (RSM) was used to optimize the process parameters of the transesterification reaction. The models showed a good agreement with the experimental results, demonstrating that this methodology was useful for optimization. The models were successful in explaining the variation of response with respect to the three process parameters studied. The fuel properties of biodiesel produced were compared with ASTM standards for biodiesel.

Keywords: Biodiesel, Transesterification, Peanut oil, Rapeseed oil, Optimization, Response surface methodology.
both saturated and polyunsaturated acids. Therefore rapeseed oil is an ideal raw material regarding combustion characteristics, oxidative stability and cold temperature behavior. Rapeseed is now second largest oilseed crop after soybean and the third largest vegetable oil, which results in a calculated yield for Rapeseed oil of 965–1342 kg·ha⁻¹·yr⁻¹ after soybean-oil and palm oil. Rapeseed contains approximately 40 wt% oil. Transesterification of rapeseed oil produces ester whose properties are comparable with those of conventional diesel fuels [15]. It has also been reported that the lubricity of diesel fuel can be enhanced by 60 % with the addition of 1 vol% canola-derived methyl ester [16].

In the present work, we report our studies on the suitability of peanut oil and rapeseed oil as a feedstock’s for biodiesel production and the influence of process parameters (catalyst concentration, type of catalyst, temperature, methanol to oil molar ratio and reaction time) in the transesterification of peanut oil and rapeseed oil using potassium hydroxide and sodium hydroxide as catalysts. Response surface methodology (RSM) was used to optimize the process parameters of the transesterification reaction. The optimal condition of the process, the relationship between process variables and the response FAME yield was calculated using response surface methodology (RSM). The properties of biodiesel were also measured and reported in this paper.

2. Experimental

2.1 Materials

Peanut oil was procured from commercial shop in Varanasi and rapeseed oil was procured from Punjab in India. Potassium hydroxide flakes, sodium hydroxide flakes, methanol and phosphoric acid were procured from Fisher Scientific, India. Methyl ester, triolein was obtained from Sigma–Aldrich, USA. All chemicals used were analytical reagents.

2.2 Experimental setup

The transesterification reaction was carried out in a batch reactor. A 500 mL three necked round bottom glass flask was used. It had provisions for a water-cooled condenser, thermometer, and mechanical stirrer. The flask was kept inside a water bath with thermostat which maintained the temperature at the desired level. The reaction mixture was stirred at 600 rpm for all test runs (Fig.1).

2.3 Transesterification

The oils were heated at 378 K for 1 h in N₂-purge to evaporate water and other volatile impurities. Heated oils were allowed to cool to room temperature. Subsequently, a desired amount of freshly prepared alcoholic solutions of catalysts were added into the oil and mixed. Each experiment was allowed to continue for a set period of time. Phosphoric acid was added to stop the reaction by neutralization of catalyst and adjust the pH of biodiesel to neutral. The reaction mixture was allowed to cool down and equilibrate which resulted in separation of two layers. The upper layer consisted of methyl esters and unconverted triglycerides. The lower layer contained glycerol, excess methanol, catalyst and any soap formed during the reaction and possibly some entrained methyl esters. After separation of the two layers by sedimentation the upper methyl esters layer was purified by distilling the residual methanol at 80 °C. The remaining catalyst was removed by successive rinses with distilled water and dried at 378 K for 4 h to remove water content from biodiesel layer.

2.4 Testing of vegetable oil and biodiesel (methyl esters) properties

Fourier-transformed infrared (FTIR) spectroscopy has been reported as a fast and accurate method to monitor the methanolysis of vegetable oils [17]. Several FTIR absorption bands (1198 cm⁻¹, 1363 cm⁻¹, 1377 cm⁻¹, 1436 cm⁻¹ and 4430 cm⁻¹) had been chosen to monitor the changes of the functional group in the canola-methanol transesterification process with base catalyst [18]. Giuliano et al. [19] studied the ethanolysis of degummed soybean oil (DSO) using Fourier-transformed mid-infrared spectroscopy (FTIR) and methods of multivariate analysis such as principal component analysis (PCA) and partial least squares regression (PLS). In the present work also, vegetable oils and methyl esters (biodiesel) were analyzed by FTIR (Thermo-Nicolet 5700 model). The spectra were obtained in the 500–4000 cm⁻¹ region, with a resolution of
4 cm$^{-1}$. Averages of 32 scans were recorded using a multi bounce ATR. The method developed by Giuliano et al. [19] was used for quantitative analysis. The height of absorbance band at wave number 1741 cm$^{-1}$ was used to calculate the concentration of ester in the biodiesel layer. A calibration plot was obtained by measuring the height of the 1741 cm$^{-1}$ bands for samples of ester and oil of known compositions. For the calibration purpose, methyl ester and triolein where taken as representative ester and oil respectively. The calibration plot thus obtained is shown in Fig.2. The yield of biodiesel was calculated using the following formula:

$$Yield = \frac{E_l}{W_o} \times E_c \quad (1)$$

Where: $E_l$, $E_c$, $W_o$ are the biodiesel layer volume in (mL), ester concentration in (g mL$^{-1}$), and weight of vegetable oil used in (g), respectively.

The samples of vegetable oil and biodiesel were tested for their fuel properties also. The flash point was determined by Cleveland open cup method using ASTM D92-53. The cloud point and the pour point were determined using cloud and pour point apparatus as specified in IP15/60. The kinematic viscosities were determined at 313K, using a Redwood viscometer as specified in ASTM D445. Calorific values were measured using a bomb calorimeter (IP12/63T). Acid values were determined by a standard titration method as specified in ASTM D664 [20]. The density at room temperature of the biodiesel was measured as specified in ASTM D4052. The Cetane index was estimated from API gravity and mid-boiling point as specified in ASTM D976.

### 2.5 Statistical analysis

The biodiesel production yield was optimized using response surface methodology (RSM) provided by STATISTICA 8 software. A standard RSM design tool known as Central Composite Design (CCD) was applied to study the transesterification reaction parameters. The central composite experimental design (CCD) is a suitable design for sequential experiments to obtain appropriate information for testing lack of fit without a large number of design points [21,22]. A two-level, three-factor central composite experimental design was used to optimize the independent variables to achieve maximum FAME yield. A total of twenty experiments, including six replications at the centre point, were conducted. The replicates at the centre point were used to evaluate the pure error. Table 1 shows the independent variables and levels used for experimental design. Three identified independent parameters are $X_1$: catalyst concentration, $X_2$: methanol to oil molar ratio and $X_3$: reaction temperature. The response chosen was biodiesel yield. The experiments were run at random in order to minimize errors from the systematic trends in the variables. The quality of fit for the model was evaluated by the coefficients of determination ($R^2$) and its regression coefficient significant (analysis of variances (ANOVA)) were checked with Fisher’s test (F-test) [22]. Response surfaces and contour plots were developed using the quadratic polynomial equation obtained from regression analysis of experimental data by keeping two of the independent variables at a constant value while changing the other one.

**Table 1. The independent variables and levels used for experimental design.**

<table>
<thead>
<tr>
<th>Code</th>
<th>Variable levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>A (Peanut oil)</td>
<td></td>
</tr>
<tr>
<td>Catalyst amount (wt %)</td>
<td>$X_1$</td>
</tr>
<tr>
<td>Methanol-to-oil molar ratio</td>
<td>$X_2$</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>$X_3$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Code</th>
<th>Variable levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>B (Rapeseed oil)</td>
<td></td>
</tr>
<tr>
<td>Catalyst amount (wt %)</td>
<td>$X_1$</td>
</tr>
<tr>
<td>Methanol-to-oil molar ratio</td>
<td>$X_2$</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>$X_3$</td>
</tr>
</tbody>
</table>
3. Results and Discussion

3.1 Effect of catalyst concentration

Figs. 3 and 4 show the effects of KOH and NaOH concentration on the transesterification of peanut oil and rapeseed oil. The concentration of KOH and NaOH were varied from 0 to 2.0 % (based on the weight of oil) and reaction time of 90 minutes was kept constant. It is observed that the maximum yield of biodiesel obtained for peanut oil and rapeseed oil at 0.5 wt% and 1 wt% catalyst concentration, respectively. The maximum yield was 95 % for peanut oil and 97 % for rapeseed oil when KOH used as catalyst. However it was only 88 % for peanut oil and 90 % for rapeseed oil in case of NaOH. The role of catalyst is vital as alcohol is barely soluble in oil or fat. The catalyst enhances the solubility of alcohol and thus increases the reaction rate [23]. The observation is related to the greater solubility of KOH and formation of methoxide.

3.2 Effect of methanol/oil molar ratio

Fig.5 shows the effect of methanol to oil molar ratio on biodiesel yield. The stoichiometric methanol to oil molar ratio required for a complete transesterification is 3:1. However, a higher molar ratio is required to drive the reaction to completion [27].

Experiments were conducted with the molar ratios 3:1, 6:1, 9:1, 12:1, 15:1, 18:1 and 21:1, respectively. The molecular weight of peanut oil and rapeseed oil calculated on the basis of fatty acid compositions were 891 and 882 g/mol, respectively. It is observed from the Fig.5 that the maximum yield of 95 % and 97 % were obtained at the methanol to oil molar ratio of 6:1 for peanut oil and rapeseed oil, respectively. Further increase in molar ratio, the yield was observed to decrease and it was only 65 % when MeOH/Oil molar ratio was 20:1. It has been reported that a higher molar ratio than the stoichiometric value results in a higher rate of ester formation [28] and could ensure complete reaction. Therefore, it is concluded that the reaction was incomplete for a molar ratio less than 6:1. The observed decrease in the yield at higher molar ratios may be due to the fact that the separation of ester layer from glycerol layer was not complete. It is known that the excess methanol hinders the separation because of the fact that methanol, with one polar hydroxyl group, can work as an emulsifier [29] and the hindrance of phase separation at higher methanol to oil ratios was also observed in the present work. Also, further increases in the methanol to oil ratio, did not promote the reaction because the catalyst content
decreased. Hence, the best results were obtained for a methanol/oil molar ratio of 6:1 in the present work. These results are in line with the reports of Meher et al. [30] and Usta [31]. They obtained high yields of esters utilizing the molar ratio of 6:1 during the methanolysis of P. pinnata and tobacco seed oil, respectively. In the ethanolation of used frying oil, Encinar et al. [32] obtained yields of 94.2 %, using an ethanol/oil molar ratio of 6:1 and 1.0 % potassium hydroxide as catalyst.

3.3 Effect of reaction temperature

In all experiments, a methanol/oil molar ratio of 6:1 and 0.5 wt% KOH in oil (as catalyst) for peanut oil, 6:1 and 1 wt% KOH in oil for rapeseed oil were used (the optimal conditions achieved in the previous section). Alkaline alcoholsysis of vegetable oils is normally performed near the boiling point of the alcohol [33]. The effect of reaction temperature (30–65 °C) on the yield was studied in the present work and the results are shown in Fig. 6.

![Figure 6. Effect of temperature on the yield of peanut oil methyl esters.](image)

The maximum yield was obtained at a temperature of 60 °C. A decrease in the yield was observed when the reaction temperature went beyond 60 °C. The literature also reports that reaction temperatures greater than 60 °C should be avoided, because it tends to accelerate saponification of the glycerides by the alkali catalyst before completion of the alcoholsysis and also, excessive loss of methanol tends to lower the yield [34].

3.4 Effect of reaction time

The effect of reaction time was also studied and it was observed that the yield becomes nearly constant at 95 % and 97 % for peanut oil and rapeseed oil, respectively after 90 minutes of reaction time as shown in Fig. 7.

![Figure 7. Effect of catalyst type on the yield of peanut oil methyl ester and rapeseed oil methyl ester.](image)

3.5 Properties of vegetable oil and methyl ester

The fuel properties of vegetable oils and corresponding biodiesels are given in Table 2. All the properties of peanut oil, rapeseed oil and corresponding product biodiesels were determined at room temperature. The peanut and rapeseed methyl esters have fuel property values relatively closer to that of mineral diesel. As compared to the mineral diesel specific gravity of 0.85, biodiesel specific gravity in the present analysis was 0.868 and 0.88, respectively. The ASTM standard D6751 prescribed an acceptable kinematic viscosity at 40 °C range for biodiesel to be 1.9–6.0 mm²/s, which was satisfied by biodiesel produced in the present work. The calorific value of methyl ester was lower than that of diesel because of their oxygen content. However, the presence of oxygen in the biodiesel may help in a complete combustion of the fuels in the engine. Cold flow properties of biodiesel are important indicators of the commercial applicability of the fuel. The key flow properties for biodiesel fuel specification are cloud and pour points. The values of cloud and pour points of peanut methyl ester produced in the present work were found to be -1 °C and 5 °C and for rapeseed methyl ester were found to be -9 °C and -3 °C. Biodiesel produced from rapeseed oil is more satisfactory than that from peanut oil because peanut oil biodiesel may have a problem in winter. A possible solution for this problem would be the use of pour and cloud point depressors [35].
According to ASTM standard D6751, no value is given for cloud and pour point. The flash point is higher than those for no. 2 diesel (85–95 °C). A higher value of flash point decreases the risk of fire. The acid value was determined using the ASTM D664. The acid value of the biodiesels produced from peanut oil and rapeseed oil were 0.45 and 0.37 mg KOH/g respectively. It is well within the specified limit of 0.8 mg KOH/g (biodiesel standard ASTM D6751). The ASTM D976 was applied for the calculation of the cetane index, giving a reasonably close approximation to cetane number. In the present analysis of peanut and rapeseed methyl esters, cetane index was 54.2 and 61.2 respectively. A typical value for mineral diesel is about 46. The cetane index is higher in biodiesel obtained from peanut oil and rapeseed oil. This parameter guarantees good control of the combustion, increasing performance and improving cold starts [36]. Thus, most of the fuel properties of peanut and rapeseed methyl esters were quite comparable to those of ASTM biodiesel standards, and therefore, the biodiesel produced from peanut oil and rapeseed oil can be used as substitute for mineral diesel.

### 3.6 Optimization of parameters

The response surface methodology was used for the optimization of parameters. Among the models that can be fitted to the response (linear, two factor interaction (2FI) and quadratic polynomial), the quadratic model was selected as it is the best model due to its highest order polynomial with significance of additional terms. The model equations based on the coded values (X₁, X₂, and X₃) as catalyst concentration, methanol/oil molar ratio and reaction temperature, respectively, for the biodiesel yield from peanut oil and rapeseed oil were expressed by Eqs. 2 and 3, respectively.

**Table 2.** The fuel properties of vegetable oils and corresponding biodiesel from vegetable oils with testing methods

<table>
<thead>
<tr>
<th>Properties</th>
<th>Peanut oil methyl ester</th>
<th>Rapeseed oil methyl ester</th>
<th>Biodiesel standard ASTM D6751-02</th>
<th>Mineral diesel standard ASTM D6751</th>
<th>Test method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinematic viscosity @ 40°C (mm²/s)</td>
<td>39.6</td>
<td>40.2</td>
<td>45.0</td>
<td>–</td>
<td>IP12/63 T</td>
</tr>
<tr>
<td>Cloud point (°C)</td>
<td>12.8</td>
<td>-4</td>
<td>5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Flash point (°C)</td>
<td>271</td>
<td>126</td>
<td>170</td>
<td>130°C</td>
<td>52</td>
</tr>
<tr>
<td>Acid value (mg KOH/g)</td>
<td>0.71</td>
<td>0.62</td>
<td>0.45</td>
<td>0.37</td>
<td>ASTM D 664</td>
</tr>
<tr>
<td>Cetane index</td>
<td>41.8</td>
<td>37.6</td>
<td>54</td>
<td>61.2</td>
<td>47 min.</td>
</tr>
</tbody>
</table>

Positive sign in front of the terms indicates synergistic effect on the FAME yield, whereas negative sign indicates antagonistic effect [37]. The result of statistical analysis of variance (ANOVA) was carried out to determine the significance and fitness of the quadratic model as well as the effect of significant individual terms and their interaction on the chosen responses. The p-value (probability of error value) is used as a tool to check the significance of each regression coefficient, which also indicates the interaction effect of each cross product. The smaller the p-value, the bigger is the significance of the corresponding coefficient [38]. In the case of model terms, the p-values less than 0.05 indicated that the particular model term was statistically significant. From the ANOVA results, the main model terms suggested that variables with significant influence on Biodiesel yield response were methanol/oil molar ratio (X₂), reaction temperature (X₃), and the interaction terms were found to exist between the main factors (X₁X₂, X₁X₃ and X₂X₃), while the significant quadratic terms were catalyst concentration (X₁²), methanol/oil molar ratio (X₂²) and reaction temperature (X₃²). The lack of fit test with p-values of 0.0521 for (Eq. 2) and 0.0532 for (Eq. 3) which were not significant (p-value>0.05 is not significant) showed that the model satisfactorily fitted to experimental data. Insignificant lack of fit is most wanted as significant lack of fit indicates that there might be contribution in the repressor-response relationship that is not accounted for by the model [39]. The predicted values versus actual values for biodiesel yield with adjusted R² values of 0.9966 for (Eq. 2) and 0.9972 for (Eq. 3) indicated that the predicted values and experimental values were in reasonable agreement (Fig. 8). It means that the data fit well with the model and give a convincingly good estimate of response for the system in the range studied. In addition, investigation on residuals was also performed to validate the adequacy of the models (Fig. 9).
The developed second-order regression models (Eqs. 2 and 3) are complex with many variables. It is difficult to understand the effect of different independent variables from the regression model, but graphical representations are easier to interpret. Contour and response surface plots were drawn to observe the effect of catalyst concentration, temperature and methanol-to-oil molar ratio on FAME yield. These plots were generated by holding one of the variables at its mid-point and varying the other two variables to obtain the response. The elliptical shape of the curves indicated a strong interaction between the variables.

Figs. 10 to 12 show that the positive effect was more significant over the negative effect; hence the conversion to FAME was increased with an increase in temperature of up to 60 °C. A further increase in temperature results in a significant negative effect due to increased evaporation rate of methanol. Fig. 9 shows the significant interaction between methanol-to-oil molar ratio and catalyst amount. The convex profile of the response surface shows a well defined optimum condition for the independent variables. Increasing the catalyst amount up to optimum value increased the FAME yield, whereas addition of more catalyst (>optimum value) resulted in poor mixing of the reaction mixture comprising solid (catalyst), non-polar (oil and FAME) and polar (methanol) phases. Hence, aggregation of catalysts and poor mass transfer between phases reduced FAME yield. Similarly, excess methanol will shift the equilibrium to the right and improve FAME yield, but beyond a certain value the excess methanol causes dilution. Catalyst concentration with respect to the volume of reaction mixture decreased with an increase in methanol concentration which then caused a drop in FAME yield.
Optimum conditions of the independent variables for the KOH catalyst transesterification of peanut oil were determined as; catalyst concentration 0.5 % by weight; reaction temperature, 60 °C; and methanol-to-oil molar ratio of 6:1 while for rapeseed oil were determined as; catalyst concentration 1 % by weight; reaction temperature, 60 °C; and methanol-to-oil molar ratio of 6:1. Therefore, it is concluded that the generated models showed reasonable predictability and sufficient accuracy for the biodiesel yield in the experimental conditions used.

4. Conclusion

From the results of the present study it is found that the optimum reaction conditions for methanolysis of peanut oil (i.e., 0.5 % KOH as catalyst, methanol/oil molar ratio 6:1, reaction temperature 60 °C, rate of mixing 600 rpm and a reaction time of 90 min), provided 95 % of biodiesel yield and for methanolysis of rapeseed oil (i.e., 1 % KOH as catalyst, methanol/oil molar ratio 6:1, reaction temperature 60°C, rate of mixing 600 rpm and a reaction time of 90 min), provided 97 % of biodiesel yield. Response surface methodology (RSM) was used to study the transesterification reaction of peanut oil and rapeseed oil for biodiesel production. The models showed a good agreement with the experimental results, demonstrating that this methodology was useful for optimization. The specific gravity, viscosity, cetane index and higher heating values of biodiesel produced under optimized protocol in the present work were similar to those of mineral diesel. However, the cloud and pour points of biodiesel produced were found to be somewhat higher, which may point to potential difficulties in cold starts and filter plugging trouble. The flash point was noted to be higher than those of mineral diesel.
References


