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Optimization of rubber seed oil extraction using liquefied dimethyl ether

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ABSTRACT

The objective of this study was to find the optimal condition for the extraction of rubber seed oil (RSO), using liquefied dimethyl ether (DME). Response surface methodology with a spherical central composite design model was employed to determine the optimal extraction condition, consisting of a seed moisture content (%wt), a solvent to solid ratio (g/g), and an extraction temperature (°C). A quadratic regression equation suggested the optimal extraction condition was a moisture content of 56.4%wt, a solvent to solid ratio of 6.7 (g/g), and a temperature of 33.3 °C. At this condition, the RSO yield predicted by the model gave a slight deviation of 0.68% from the experimentally validated results (41.48 versus 41.20%). RSO has a kinematic viscosity of 36.8 cSt, an acid value of 10.7 KOH/g oil, a fatty acid content of 5.1% and an unsaturated fatty acid content of 80%, resulting in the potential production of biodiesel, biolubricants, and biodegradable plastics.

KEYWORDS

Biofuels; Rubber seed oil; Extraction; Dimethyl ether; Optimization; Response surface

1. Introduction

Rubber trees (*Hevea brasiliensis*), despite their Amazon rainforest origin, are now grown extensively for natural rubber production in many Asian countries, including Thailand, Indonesia, Malaysia, India, and China. In the rainy season, each rubber tree produces about 5 kg of fresh rubber seeds, each weighing 3–6 g, consisting of 42–51% shell and 49–58% kernel. Fresh rubber seeds, especially the kernels, have a very high moisture content of ~29–50%wt, which is equal to a 40–100% dry basis (Widyarani et al., 2014). When dried, the rubber seeds have been reported to contain as much as 40–60% oil (Ikwuagwu et al., 2000; Ramadhas et al., 2005a, 2005b, 2005c). However, due to the presence of poisonous hydrogen cyanide, rubber seed oil (RSO) is non-edible (Salimon et al., 2012). Being a nonedible oil makes RSO more suitable for economical feedstock for various industrial applications than edible oils, such as palm and coconut oil. Owing to its chemical composition and physico-chemical properties, such as kinematic viscosity, flash point and cloud point, RSO is suitable for the production of biodiesel, biolubricants, and biodegradable plastics (Ikwuagwu et al., 2000; Ramadhas et al., 2005a, 2005b, 2005c; Kamalakar et al., 2013; Khazaai et al., 2017; Kynadi and Suchithra, 2017).

To recover oil from rubber seeds, various extraction techniques can be applied. The simplest oil extraction is by a mechanical press, but it is reported to give low RSO yields (Herry et al., 2014). Extraction using a non-polar organic solvent, such as hexane or petroleum ether, gives a higher yield of oil (Ali et al., 2015), although this requires energy-intensive steps for removal of the toxic solvent (i.e., by evaporation). Alternatively, extraction with supercritical carbon dioxide (SC-CO_2) allows the solvent to be separated readily by depressurizing the system. Unfortunately, this process utilizes high pressures, leading to high equipment and operating costs (Fiori, 2010; Xiang et al., 2011; Lee et al., 2013),

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which make the process uneconomical in many cases. Moreover, the extraction of oil from fresh rubber seeds with nonpolar organic solvents, including SC-CO_2, gives a low yield, due to a lack of accessibility of the solvents into the relatively wet seeds (Tallon and Fenton, 2010). The oil yield can generally be improved by drying the raw seeds prior to extraction, but the drying process is extremely energy intensive.

Recently, liquefied dimethyl ether (DME), a chemical widely used as a fuel, an aerosol propellant, an assistant solvent, a vesicant and a refrigerant (Jianguo et al., 2011), has been reported to be an effective solvent for extraction of lipid and active compounds from various natural materials (Tallon et al., 2007, 2008; Catchpole et al., 2010; Kanda et al., 2012; Li et al., 2014; Boonnoun et al., 2017). When compared to other organic solvents, DME is a nontoxic solvent for extraction. In addition, DME is considered a green solvent since it has zero ozone depletion potential and low global warming potential (Azizi et al., 2014). DME can also be easily removed from the final product in a similar manner as in SC-CO_2 extraction by depressurizing the system. However, extraction with DME has an advantage over SC-CO_2 extraction in that it requires a lower extraction pressure of ~1 MPa (or 20–60 times lower pressure) (Kanda et al., 2012; Lee et al., 2013; Li et al., 2014). In addition, DME is partially miscible with water (Pozo and Streett, 1984; Holldorff and Knapp, 1988), and so has been successfully applied for extraction of high moisture content materials without requiring prior drying (Tallon et al., 2007, 2008; Catchpole et al., 2010; Kanda et al., 2012; Li et al., 2014; Boonnoun et al., 2017).

This study therefore focused on the investigation of RSO extraction using liquefied DME. Response surface methodology (RSM) with a spherical central composite design (CCD) was employed for the optimization of process variables (seed moisture content, solvent to solid weight ratio, and extraction temperature) to obtain the maximum RSO yield. The RSO obtained was then characterized by determining its physico-chemical properties.

2. Materials and methods

2.1. Materials and chemicals

Fresh rubber seeds were obtained from a local farm in Phitsanulok Province, Thailand. The rubber seeds were manually peeled to collect only the inner white kernels. The kernels were weighed and then cut into rough pieces and dried in a hot air oven at 60 °C for 72 h. The dried kernels were then weighed to determine the moisture content of the starting kernels, which was found to be ~86% on a dry basis. The dried sample was grounded with an electric grinder to obtain ~40–60 mesh kernel sample and then stored in a desiccator until extraction to prevent the ground sample from absorbing moisture. The liquefied DME (Spray Work Air Can 420D) used for extraction was purchased from Siam Tamiya Co., Ltd., Thailand and hexane (purity >99.5%) was purchased by Sigma-Aldrich.

2.2. RSO extraction with liquefied DME

DME extraction was carried out using the apparatus and procedure described in our previous work (Boonnoun et al., 2017). Briefly, ~10 g of the dried ground kernel sample was firstly mixed with an exact amount of distilled water to achieve the desired moisture content on a dry basis. The sample was then loaded into a cellulose thimble (30 × 100 mm) along with an 8-mm-diameter magnetic bar, which was placed into an extractor (100-ml stainless-steel). To achieve the required solvent to solid weight ratio (g/g), liquefied DME was added through a needle valve into the preweighed extractor. Subsequently the extraction was conducted at a controlled temperature, under constant stirring at 500 rpm for 30 min. After extraction, the liquid containing DME and the extracts were transferred through a stainless-steel filter (7 μm pore diameter, Swagelok, Thailand) to a 100-ml beaker. Water extracted into this liquid was then dried using a hot plate stirrer at 120 °C for 15 min. The resulting oil was weighed to determine the oil yield based on dried kernel weight.

To compare DME extraction with hexane extraction, 10 g of dried kernel flakes were extracted with 200 ml of hexane using a Soxhlet apparatus for 18 h.

2.3. Experimental design and optimization of extraction condition using RSM

RSM with the spherical CCD model was used to determine the optimal extraction condition. Three extraction parameters were defined as seed moisture content = X_1 (%wt in dry basis), solvent to solid weight ratio = X_2 (g/g) and extraction temperature = X_3 (°C). The value of α for the CCD was defined as $\alpha = \sqrt{K}$ where K is the number of parameters ($K = 3$), so the α values used in this study were −1.73 and +1.73. The low, middle, and high levels of each parameter were therefore designated as −1, 0, and +1, respectively. The corresponding actual values for each parameter are shown in Table 1. The correlation between the parameters and the response is described by Equation (1), as follows:

$$\text{Yield} = \beta_0 + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X^2{}_i + \sum_{i=1}^{3} \sum_{i=1}^{3} \beta_{ij} X_i X_j \quad (1)$$

Where X_i = actual parameter values, β_0 = interception, β_{ii} = regression coefficient, and β_{ij} = cross product coefficient.

The analysis of the spherical CCD experimental design, analysis of variance (ANOVA) and optimization of the condition were carried out using Minitab Statistical Software (version 17).

Table 1. Levels of actual and coded factors.

X_i	−1.73	−1	0	1	1.73
Moisture content (%wt)	5.5	20	40	60	75
Solvent to solid weight ratio (g/g)	3.3	4	5	6	6.7
Temperature (°C)	31	35	40	45	49

2.4. Characterization of RSO

To determine its characteristics, RSO obtained at the optimal condition was characterized using FT-IR and ^{1}H NMR analysis. FT-IR was conducted using an FT-IR instrument (Perkin Elmer Frontier) following the method described by Ali et al. (2015) and Aigbodion and Bakare (2005). ^{1}H NMR spectra of the RSO were obtained by a 600 MHz NMR spectrometer (Avance-II Ultrashield-400 MHz, Bruker) using a 5-mm-diameter NMR tube according to the procedure described by Ali et al. (2015) and Aigbodion and Bakare (2005). Physico-chemical properties including kinematic viscosity, acid value and % fatty acid of RSO were determined following standard methods of ASTM D445, AOCS (Te 1a-64), and AOCS (Te 1a-64), respectively. The fatty acid composition was determined according to ISO 5508 using gas chromatography (GC-FID detector, Shimadzu 2010 model).

3. Results and discussion

3.1. Experimental design and optimization of extraction condition

3.1.1. Quadratic regression model and variance analysis

The 17 sets of operating conditions with their corresponding experimental RSO yields as well as their model-predicted yields are shown in Table 2. The ANOVA values for the quadratic regression equation and the significance of regression coefficients from the spherical CCD are shown in

Table 2. Spherical CCD experimental parameters, experimental, and predicted data.

Run	Moisture content (%wt) (X_1)	Solvent to solid weight ratio (g/g) (X_2)	Temperature (°C) (X_3)	Experimental %Yield (g oil/g dried seed)	Predicted %Yield (g oil/g dried seed)
1	20	4	35	15.57	16.90
2	60	4	35	29.90	28.21
3	20	6	35	32.99	33.43
4	60	6	35	37.63	40.82
5	20	4	45	23.40	22.86
6	60	4	45	26.39	28.61
7	20	6	45	27.84	32.17
8	60	6	45	32.68	34.00
9	5.5	5	40	24.85	23.23
10	75	5	40	35.98	34.61
11	40	3.3	40	18.66	19.55
12	40	6.7	40	42.37	38.51
13	40	5	31	31.34	30.98
14	40	5	49	32.58	30.21
15	40	5	40	35.88	35.41
16	40	5	40	33.81	35.41
17	40	5	40	36.39	35.41

Table 3. From these results, the predicted data from the quadratic regression equation was fitted to the experimental data, which showed an R^2 value of 0.9135 and an adjusted R^2 value of 0.802. The RSM suggested a quadratic equation with an F-value of 8.21 and a p-value of 0.006. The significantly lower p-value compared to the F-value indicated that the model was acceptable. The ANOVA revealed the p-values of seed moisture content (X_1) and solvent to solid weight ratio (X_2) were 0.005 and <0.0001, respectively. These two values indicate that seed moisture content and solvent to solid weight ratio affected the RSO yield significantly. The quadratic polynomial equation with substituted actual parameter values is shown in Equation (2), as follows:

$$\begin{aligned}\text{Yield} = &-268.0 + 1.399X_1 + 43.2X_2 + 7.57X_3 \\ &-0.00541{X_1}^2 - 2.128{X_2}^2 - 0.0658{X_3}^2 \\ &-0.0490X_1X_2 - 0.0139X_1X_3 - 0.361X_2X_3 \quad (2)\end{aligned}$$

where X_1, X_2, and X_3 are parameters in actual values.

3.1.2. Interactions among process variables

The interaction among process variables including moisture content, solvent to solid weight ratio, and extraction temperature were investigated from the 3D surface and contour plots generated by the quadratic equation as shown in Figures 1–3. The effect of moisture content and solvent to solid weight ratio on RSO yield at an extraction temperature of 40 °C is shown in Figure 1. The results revealed that a higher seed moisture content resulted in a higher RSO yield. One possible explanation is that the presence of water could act as a cosolvent for oil extraction leading to the increased RSO yield. Similar results were also observed in previous research (Tallon et al., 2008), which indicated that the presence of water in the seed is necessary for oil extraction using DME. However, it is worth noting that an excessive amount of water might increase overall solvent polarity and potentially cause a lower oil yield. Moreover, an increase in solvent to solid weight ratio significantly increased RSO yield. These results might be explained by the fact that solute-solvent interactions are known to be enhanced by an increase in solvent amount. It follows that increased DME would thus enhance the RSO extraction and solubilization into the DME.

Table 3. ANOVA for the quadratic regression equation.

Source	Sum of Square	df	Mean Square	F-value	p-value
Model	714.515	9	79.931	8.21	0.006*
X_1	151.73	1	151.73	15.69	0.005*
X_2	422.786	1	422.786	43.72	<0.0001*
X_3	0.944	1	0.944	0.1	0.764
X_1X_2	7.675	1	7.675	0.79	0.403
X_1X_3	15.496	1	15.496	1.6	0.246
X_2X_3	26.043	1	26.043	2.69	0.145
X_1X_1	56.818	1	56.818	5.88	0.046*
X_2X_2	55.015	1	55.015	5.69	0.049*
X_3X_3	32.906	1	32.906	3.4	0.108
Error	67.698	7	9.671		
Total	782.213	16			
R^2	0.9135				
Adjusted R^2	0.802				

*The parameters significantly affect RSO yield (p-value <0.05).

The effect of seed moisture content and extraction temperature on RSO yield at a solvent to solid weight ratio of 5:1 (g/g) is shown in Figure 2. As in the previous results, the increase in seed moisture content gave a higher RSO yield. Increasing the extraction temperature initially increased the RSO yield, but this decreased as the temperature rose above 38 °C. Increasing the extraction temperature generally increases oil solubility into the solvents; however, the DME density is also known to decrease at high temperatures (Ihmels and Lemmon, 2007) and this decrease results in a lower solvent efficacy. At higher extraction temperatures, the decrease in solvent efficacy may outpace the increase in solubility of the RSO into the DME, resulting in a lower RSO yield.

The effect of solvent to solid weight ratio and extraction temperature on RSO yield at a seed moisture content of 40%wt is shown in Figure 3. Similar trends to the results shown in Figures 1 and 2 were also observed. The increase in solvent to solid weight ratio increased the RSO yield. Increasing the extraction temperature from 30 to 38 °C increased the RSO yield but the yield decreased at the higher extraction temperatures.

3.1.3. Model validation

The regression model's suggested optimal extraction condition to obtain the maximum RSO yield of 41.48% were a seed moisture content of 56.4%wt, a solvent to solid ratio of 6.7 (g/g), and

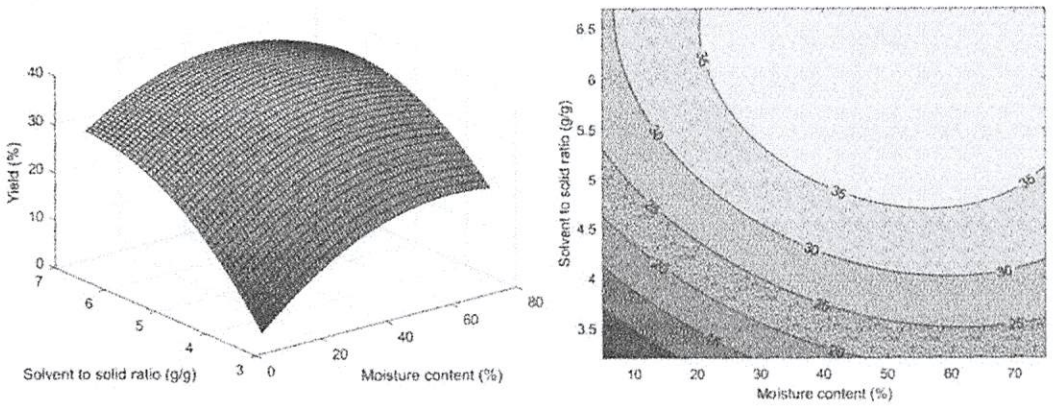

Figure 1. 3D surface and contour plots explaining the interaction effects of moisture content (X_1) and solvent to solid ratio (X_2).

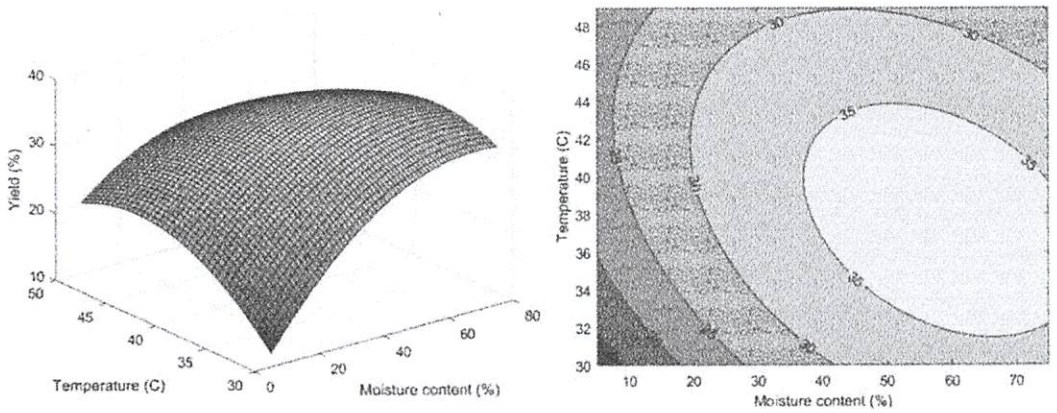

Figure 2. 3D surface and contour plots explaining the interaction effects of moisture content (X_1) and temperature (X_3).

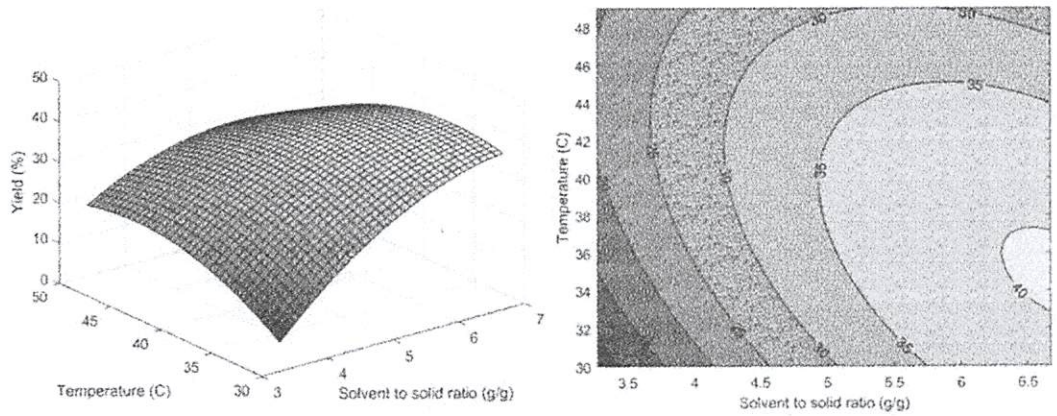

Figure 3. 3D surface and contour plots explaining the interaction effects of solvent to solid ratio (X_2) and temperature (X_3).

a temperature of 33.3 °C. These values were rounded to 56%wt, 6.7, and 33 °C, respectively, and the experiment was conducted in triplicate. The actual RSO yield obtained was 41.20 ± 0.87%, which showed that the regression equation's RSO yield prediction was reasonable (0.68% deviation).

Compared with Soxhlet extraction using hexane as solvent, DME extraction gave a slightly lower RSO yield (41.20 ± 0.87% versus 44.5%). However, the extraction process using liquefied DME theoretically requires lower energy consumption. DME extraction does not require completely dried rubber seeds to optimize oil yield

but a suitable moisture content of 56% should be maintained. Moreover, the differences in RSO yield that resulted from varying extraction temperature in the range of 30–50 °C were not statistically significant, since the p-value for temperature (X_3) was >0.05 (as seen in Table 3). Therefore DME extraction, at least at the local room temperature (~30–45 °C), requires no additional energy input to optimize the RSO yield. The results indicate that liquefied DME has potential to be used for recovery of RSO.

3.2. Characterization of RSO

RSO obtained at the optimum extraction condition was characterized to determine its chemical characteristics by FT-IR and ^{1}H NMR analysis. The FT-IR spectrum of RSO is shown in Supplementary Material Figure S1. The main peaks and their corresponding functional groups are given in Table 4. The main component in RSO was found to be triglyceride, which can be observed in Supplementary Material Figure S1 as a strong absorption band of the ester carbonyl functional group at 1742 cm^{-1}. The FT-IR spectrum in this work also showed a fingerprint region of RSO seen at 1458–587 cm^{-1} (Onoji et al., 2016).

The signal assignments of RSO obtained from ^{1}H NMR analysis are shown in Table 5 and Supplementary Material Figure S2. RSO structure consists of terminal methyl in the FA chain at 0.859–0.979 ppm, with methylene groups next to the terminal methyl at 1.597 ppm; these methylene groups have one double bond at 1.989–2.061 ppm, and two double bonds at 2.739–2.79 ppm. Other groups are a carbon-carbon double bond (C = C) and methylene of glyceryl (α = 4.137–4.152 ppm and β = 5.309–5.369 ppm).

The physico-chemical properties of DME extracted RSO are reported in Table 6. The results show that the RSO had a golden yellow color, a kinematic viscosity of 36.8 cSt, an acid value of 10.7 KOH/g oil, and a fatty acid content of 5.1%. The fatty acid content of RSO obtained by liquefied DME extraction was lower than the extraction using other organic solvents reported in previous work of Wuttichai et al. (2017). The results revealed that fatty acid contents of RSO extracted by hexane, acetone, dichloromethane, and ethyl acetate were 5.2%, 10.1%, 11.8%, and 8.1%, respectively (Wuttichai et al., 2017). Despite the lower fatty acid content of RSO in this work, which might be caused by the differences in growth conditions, it can be implied that the low fatty acid content of the RSO suggests its use for biodiesel production. When using alkali-catalyzed transesterification, fatty acid content must be minimized to avoid a side saponification reaction. When compared to *Jatropha* oil, RSO has a slightly higher fatty acid content (5.02% versus 3.3%) (Talita et al., 2015). However, rubber seeds are more attractive than *Jatropha* because of their higher oil content (40–69% versus 17–36%) (Talita et al., 2015). In addition, the RSO obtained in this work also showed possibility for use in the production of biolubricants due to its kinematic viscosity, which was in the range of standard lubricants [viscosity grade: 22 (at 40 °C = 19.2–24.2 cSt, at 100 °C ≤ 4 cSt)] (Kamalakar et al., 2013).

Moreover, RSO's fatty acid profile as determined by GC analysis is shown in Table 7. The

Table 4. Main peaks in the FT-IR spectra of RSO.

Peak (cm^{-1})	Functional group
3009	=C–H stretching of nonconjugated (methylene group)
2921–2852	C–H stretching vibration (methyl group)
1742	–C = O stretching vibration (carbonyl)
Fingerprint region (1435–585 cm^{-1})	
1458	C–H bending frequency (alkene)
1377	C–H bending vibration (alkene)
1236	C–O stretching vibration (Carboxylic acids, ester)
1159	C–O stretching vibration (ester)
1097	=C–O–C stretching vibration (ester)
721	C–H bending vibration (aromatic)
587	C–H vibration (alkane)

Table 5. Signals present in ^{1}H NMR spectra of RSO and their assignment.

δ (ppm)	Assignment
0.859–0.979	$-CH_3$ terminal methyl
1.244–1.358	$-CH_2$ saturated aliphatic chain
1.597	$-CH_2-C$ methylene α to terminal methyl
1.989–2.061	$-CH_2-C=C$ allylic methylene
2.275–2.319	$-CH_2-O-C=O$ acyl methylene
2.739–2.79	$-C=C-CH_2-C=C-$ diallylic methylene
4.137–4.152	$-CH_2-O-CO-$ in α position in glyceryl
4.265–4.275	$-CH=CH-$ olefinic (FA chain)
5.309–5.369	$-CH-O-CO-$ in β position in glyceryl

Table 6. Physico-chemical properties of RSO.

Properties	RSO	Testing methods
Color	Golden yellow	
Kinematic viscosity (Cst at 25 °C)	36.8	ASTM (D445)
Acid value (mg of KOH/g oil)	10.7	AOCS (Te 1a-64)
Free fatty acid (%)	5.1	AOCS (Te 1a-64)

Table 7. Fatty acid composition of RSO.

Fatty acid	Percentage
Unsaturated fatty acid	80.01
Linoleic acid	41.21
Linolenic acid	15.25
Oleic acid	23.1
Palmitoleic acid	0.29
Elcosenoic acid	0.16
Saturated fatty acid	15.59
Myristic acid	0.12
Stearic acid	6.39
Palmitic acid	8.8
Arachidic acid	0.28

results revealed an RSO total unsaturated fatty acid content of 80.01%. The unsaturated fatty acids were identified as 41.21% linoleic, 15.25% linolenic, and 23.10% oleic acids. The total saturated fatty acid content was found to be 15.59%. The main saturated fatty acid of RSO was palmitic acid (8.80%). These results suggested that the DME extracted RSO is also suitable for use as a feedstock in the biosynthesis of polyhydroxyalkanoates, a starting material for biodegradable plastic production, because the bacteria used for plastic biosynthesis favorably utilizes oil with high unsaturated fatty acid content (Kynadi and Suchithra, 2017).

4. Conclusions

Liquefied DME was found to be an effective solvent for RSO extraction. The maximum RSO yield of 41.20% could be achieved at a 56%wt seed moisture content, a 6.7 solvent to solid ratio and a 33 °C extraction temperature, which were reasonably predicted by RSM. The physico-chemical properties of the RSO were found to be a kinematic viscosity of 36.8 cSt, an acid value of 10.7 KOH/g oil, a fatty acid content of 5.1%, and an unsaturated fatty acid content of 80%. This current research provides a means for energy conservation in the process of DME extraction of oil from high moisture content rubber seeds. The obtained RSO could be considered as a feedstock for industrial applications, including production of biodiesel, biolubricants, and biodegradable plastics.

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