Manuscript submitted to: Volume 2, Issue 2, 193-209.

AIMS Energy DOI: 10.3934/energy.2014.2.193

Received date 20 March 2014, Accepted date 13 June 2014, Published date 20 June 2014

Research article

First stage of bio-jet fuel production : non-food sunflower oil extraction using cold press method

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Abstract: As a result of concerning petroleum price increasing and environmental impact, more attention is attracted to renewable resources for transportation fuels. Because not conflict with human and animal food resources, non-food vegetable oils are promising sources for developing bio-jet fuels. Extracting vegetable oil from oilseeds is the first critical step in the pathway of bio-jet fuel production. When sunflower seeds are de-hulled, there are always about 5%–15% broken seed kernels (fine meat particles) left over as residual wastes with oil content up to 48%. However, the oil extracted from these sunflower seed residues is non-edible due to its quality not meeting food standards. Genetically modified sunflower grown on margin lands has been identified one of sustainable biofuel sources since it doesn't compete to arable land uses. Sunflower oils extraction from non-food sunflower seeds, sunflower meats, and fine sunflower meats (seed de-hulling residue) was carried out using a cold press method in this study. Characterization of the sunflower oils produced was performed. The effect of cold press rotary frequency on oil recovery and quality was discussed. The results show that higher oil recovery was obtained at lower rotary frequencies. The highest oil recovery for sunflower seeds, sunflower meats, and fine sunflower meats in the tests were 75.67%, 89.74% and 83.19% respectively. The cold press operating conditions had minor influence on the sunflower oil quality. Sunflower meat oils produced at 15 Hz were preliminarily upgraded and distilled. The properties of the upgraded sunflower oils were improved. Though further study is needed for the improvement of processing cost and oil recovery, cold press has shown promising to extract oil from non-food sunflower seeds for future bio-jet fuel production.

Keywords: Sunflower oilseeds; Vegetable oil; Jet fuel; Frequency; Catalyst

1. Introduction

Aviation fuel is very costly fuel in the markets, especially, those used in military jets, such as "Jet A" jet for the U.S. navy and air force. Almost all jet fuels are currently produced from petroleum. It is very important to find a sustainable and affordable alternative for jet fuel production due to concerning petroleum limitations including finite reserve, greenhouse gas emission, and continually increasing price. Biomass-derived jet fuel (also called bio-jet fuel) can be an alternative to petroleum fuels with less impact on environment [1-4]. Non-food vegetable oils (simply called vegetable oils in the study, unless specified) may be a promising alternative to petroleum-derived jet fuels because of their benefits of less impact on environment and not competing to human and animal food sources [5-8].

The advantages of using these vegetable oils for bio-jet fuels production include physicochemical properties closed to fuels, current availability, high energy density, less water content, and relative inexpensiveness and stability. Also, the liquid nature of those vegetable oils is convenient for processing and transportation [9,10]. Throughout the world, large amounts of non-food vegetable oils are available. Generally, these non-edible oil sources can be classified to three categories: non-edible plant oils (e.g. jatropha tree, linseed, microalgae, etc.), waste cooking oils, and the oils or wastes produced from edible oilseeds processing. For example, sunflower is a typical edible oil crop. When sunflower seeds are de-hulled, there are always about 5%–15% broken seed kernels (fine meat particles) left over as residual wastes with high oil content up to about 48%. However, the oil extracted from these residues is non-edible due to its quality not meeting food standards. Another example is that genetically modified sunflower grown on margin lands has been identified one of sustainable biofuel sources since it doesn't compete to arable land uses. Although these margin lands are largely unproductive or located in poverty-stricken areas and in degraded forests, the sunflower plants are well adapted to arid, semi-arid conditions and require low fertility and moisture demand to grow on the lands such as cultivators' field boundaries, fallow lands, old mining lands, and in public lands such as along railways, roads and irrigation canals. Due to their widespread production and high yield, those sunflower seeds are considered being important renewable energy sources [11-14]. South Dakota ranked the number one on the production of sunflower seeds in the United States with an annual production of 777 million pounds in 2011 [15]. It is estimated there will be about 80 million pounds of sunflower seed residues available for biofuel production. Kephart et al. had analyzed the feasibility of sunflower and other feedstock development in the North Central region of the United States. There are many researchers working on the research of converting vegetable oils into jet fuels to achieve a production goal of approximately 2.24 million gallons of JP-5 bio-jet fuel for the U.S. Navy in 2016 [16].

Various technologies are under developing to convert vegetable oils into bio-jet fuels. Transesterification is one method to refine the product oils into fuels. In the transesterification of vegetable oils, triglycerides generally react with methanol or ethanol to produce glycerol and esters. However, transesterification is usually used to produce biodiesel [17,18]. Thermal cracking involves either carbonium ion or the free radical mechanism during the thermal decomposition of oils. However, the yield of gasoline is relatively lower compared to catalytic cracking [19]. In hydrothermal catalytic cracking process, the introduction of hydrogen could help removing oxygen atom as the form of H_2O. However, the price of hydrogen is high and it is dangerous at high pressure [20,21,22]. Although various technologies have been explored to convert vegetable oils to jet fuels in recent years, catalytic cracking was found one of the most promising processes because of its high

yield of quality hydrocarbon fuels, high conversion efficiency, and low processing cost. During catalytic cracking, vegetable oil first undergoes thermal and catalytic cracking on the external surface of catalysts to produce heavy hydrocarbons and oxygenates. These products were further cracked into light alkenes and alkanes, water, carbon dioxide and carbon monoxide by tandem catalysis (one-pot reactions) without intermediate isolations. The quality and yield of target products are heavily relied on vegetable oil properties, catalyst applications, and reactor performance [23].

Extracting high quality vegetable oil from oilseeds is the first critical step for bio-jet fuel production. Vegetable oil compositions may vary with the species, variety, and the environmental conditions, under which the oilseed crop is grown, as well as the extraction methods and processing conditions applied [24,25]. There are different proven vegetable oil extraction technologies available, such as distillation, maceration, dissolving by volatile solvents, pressing/expeller, solvent extraction, and cold pressing/expeller, but most of them are used for edible vegetable oil extraction. Each of these technologies has advantages and limitations in terms of oil yield, efficiency, and processing costs [26]. Very fewer technologies have been used in non-food vegetable oil production for bio-jet fuel use. It is necessary to explore a cost effective process for efficiently extracting non-food vegetable oils from different non-food oilseeds.

Cold press method has many advantages for vegetable oil extraction. First, cold press machines can process vegetable oils continuously with minimal labor. Second, the use of cold press has low capital cost. Cold press technique is suitable to be used in rural areas, where small-scale extraction of oilseeds is required. However, solvent extraction and steam distillation technology are costly compared to cold press [27]. Third, cold press has high oil recovery under low temperature with very little impact on the oil quality. Cold press has similar concentration of fatty acids in oil extracted from seeds to other three techniques, including solvent extraction using petroleum-ether, aqueous extraction and supercritical fluid extraction using carbon dioxide (SCFE CO_2) [28]. Fourth, Cold press processing residual meals could be easily used as feed for animals.

The goal of this study is to explore a cost effective process of oil extraction from non-food sunflower seeds and meats. In the present work, sunflower oil extraction from non-food sunflower seeds with hulls, sunflower meats without hulls, and fine sunflower meats produced from sunflower seeds de-hulling will be conducted using a cold press process. The sunflower oils produced will be characterized. The cold press performance will also be evaluated. The specific objective of this study is to examine the effects of frequency that controls screw rotating speed and processing temperature on the produced sunflower oil properties, such as pH value, moisture content, density, viscosity, chemical composition, CHNO contents, and then optimize processing conditions, eventually, provide information for development of a cost effective process that can efficiently extract vegetable oils from various non-food oilseeds for bio-jet fuel production in the future.

2. Materials and methods

2.1. Material preparation

The feedstocks, sunflower seeds (SS), sunflower meats (SM), and fine sunflower meats (FSM) were purchased from a local company, Sunbird Inc., Huron, South Dakota, USA. The pictures of SS, SM, and FSM are shown in Figure 1. SM were the pure sunflower kernels after SS de-hulling. FSM

are the residual wastes produced from SS de-hulling, which may contain some small broken hull particles. All these feedstocks were packed in bags and delivered to our biofuel laboratory. The bags were sealed and stored in our lab at room temperature for about three month before sunflower oils extraction started. There were no rancid smell or spoiling SS, SM, and FSM found during the oil extraction trials. These feedstocks had good quality prior the tests. Table 1 lists the particle size, bulk density, and moisture content of the sunflower seeds and meats. The length and width of seed or meat samples were measured based on the ASTM D 4791 standard. The length means the maximum dimension of particles and the width refers to the maximum dimension in the plane perpendicular to the length. The particle size was tested using a proportional caliper. The moisture contents of sunflower seeds and meats were determined by following the ASABE biomass water content measurement standards. The samples were put in an oven and then dried at 105 °C for 24 hours. After that, the dried samples were weighed to calculate the water content in the sunflower seeds or meats [29]. All of the prepared feedstocks were used for the cold press tests directly without other pretreatment.

(a) **(b)** **(c)**

Figure 1. Pictures of (a) SS, (b) SM, and (c) FSM.

Table 1. Physical properties of the sunflower seeds and meats.

Type of sources	Length (mm)	Width (mm)	Bulk density (g/mL)	Moisture content (wt. %)
SS	7.94–12.7	3.18–6.35	0.459 ± 0.008	5.43 ± 0.124
SM	6.85–11.6	2.25–6.01	0.603 ± 0.004	2.84 ± 0.069
FSM	≤ 6.35	≤ 3.18	0.568 ± 0.005	3.34 ± 0.260

2.2. Experimental design

A M70 Oil Press was purchased from Oil Press Company, Eau Claire, Wisconsin, USA, for the sunflower oil extraction tests. To examine the feasibility of cold press technology for producing high yield and good quality vegetable oils, the tests of oil extraction from SS, SM and FSM were carried out at different conditions using the M70 Oil Press. This machine mainly consists of a nozzle set

with different sizes (1), a heat bond (2), a screw, a blast gate (4), a gear box (6) and a motor (7), as shown in Figure 2. The sunflower oilseeds and meats were pressed at different temperatures with three frequencies, 15 Hz, 20 Hz, and 25 Hz respectively, which were controlled by a variable frequency drive (VFD). The pressure inside the screw was adjusted by adding washers at the end of the screw. Oil press machine was preheated to the setting temperature of 100 °C. The screw was started to run at the setting frequency controlled by the VFD. After the temperature and rotating speed became stable, sunflower seeds or meats were fed in the screw through the blast gate. The processing temperature was controlled between 98.0 °C and 112.4 °C when the extrusion became stable. The sunflower seeds or meats were broken and compressed by the screw. Oils were forced out of the sunflower seeds or meats through the steel press meshes. The heat produced by the screw friction made the oils flow better. Each feedstock sample would be tested at the three selected frequencies. The test was duplicated. A total of 9 tests were needed for the study. The processing residual meals were extruded out through the nozzle at the front of the screw. The oil remaining in the meals was determined by solvent extraction using N-hexane. SM oils produced by the cold pressed at 15 Hz were catalytically cracked in a tubular fixed-fed reactor at 600 °C. HZSM-5 was used as catalyst and nitrogen was used as carried gas in the reactor [30]. The nitrogen pressure was 20 psi with the liquid hourly space velocity of 3 h^{-1}. The refrigerated circulator's temperature was set as –10.0 °C for cooling and collecting the fuel. After being obtained from upgrading process, the drop-in fuel (DIF) was distilled at 220 °C to further improve the quality. The distillation fuel (DF) was collected.

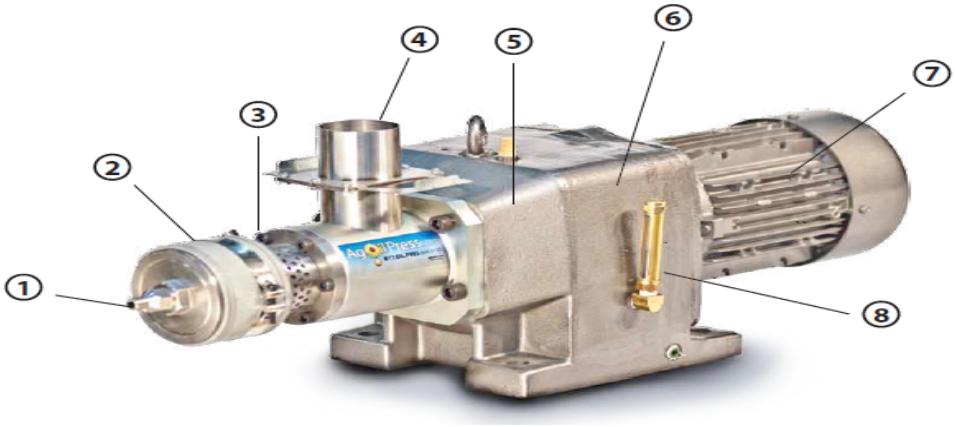


Figure 2. M70 Oil Press

2.3. Data collection

N-hexane with purity of 95% was purchased from Fisher Scientific, New Jersey, USA, for determination of residual oil content in the processing meal after sunflower oil extraction, and for Gas Chromatography-Mass Spectrometry (GC-MS) sample preparation. PH value of the vegetable oil samples were measured by using a pH meter (Accumet BASIC AB15, Fisher Scientific) at 20 °C. The dynamic viscosity was determined by using a Viscoanalyzer (REOLOGICA Instruments AB Company) at 20 °C. Moisture contents of the vegetable oil were measured by using a Karl Fischer Titrator V20 (Mettler Toledo Company) at room temperature. Methanol was used as solvent. CombiTitrant 5 Keto (for Volumetric Karl Fischer Titration) was used as detecting agent in this

measurement. The density of vegetable oils was measured by weighing the mass of the sample in a certain volume, and then the density was obtained by the oil mass divided by the volume. Each measurement was triplicated. The average of the three tests was used to represent the density of the oil sample [5]. The heating value was tested by using a Calorimeter System (C 2000, IKA-Works, Inc.).

The major chemical compounds of oil samples were identified by using a GC-MS (Agilent GC-7890A and MSD-5975C). The fatty acid profile of oil largely influences the fuel properties [31]. N-hexane with purity of 95% was used as the solvent for the preparation of samples for GC/MS test. The capillary column was 30 m × 0.25 mm × 0.25 μm DB-5MS. Hydrogen was used as the carrier gas and the flow rate was held constantly at 1 mL/min. One μm oil was introduced through the injection port operated in a splitless mode at the GC oven temperature of 285 °C. The splitless time was 30 sec. The original column temperature was 175 °C and then became 270 °C after 6 min at a speed rate of 15 °C/min. The holding time was 15.68 min. The total run time was 28 min [32].

Carbon (C), hydrogen (H), nitrogen (N), and oxygen (O) contents of vegetable oil were determined by using an EA440 Elemental Analyzer. The tests were performed by the technician at the Exeter Analytical Inc., North Chelmsford, MA, USA. For CHN content analysis, the combustion temperature was 980 °C and the time was set as 20 sec. The reduction temperature was 650 °C. The purge time was 15 sec. The oxygen pressure was 20 psi with sealed tin capsules in nickel sleeves. Acetanilide was used as the calibration standard. For oxygen content analysis, the combustion temperature and reduction temperature were 950 °C and 670 °C respectively. The combustion time was 40 sec and the purge time was 50 sec. The samples were added in sealed silver capsules without oxygen pressure. The calibration standard used was acetanilide [33].

The oil content of the processing residual meals was determined by using a solvent extraction method. An Accelerated Solvent Extractor (Dionex ASE 350, Thermo Scientific Company) was used to run the solvent extraction tests. When solvent extraction was carried out, about 12 g of residual meal was taken. 105 °C of oven temperature and 50% of rinse volume were selected. Hexane was used as solvent. The static time and purge time were 10 min and 60 sec respectively. There are three static cycles. The meal sample was mixed with the solvent and put into the ASE extractor to dissolve the oil inside the meal. After the oil was dissolved, the mixture solution of oil and solvent was separated from the solid meal. The oil content of residual meal was obtained by separating the oil from the mixture solution using a distillation processing. The tests of oil content measurement for each sample were triplicated [10,34].

3. Results and discussion

3.1. Oil extraction recovery

Figure 3 shows the oil extraction recovery of cold pressing sunflower seeds and meats at different rotating frequencies. During the SS extraction trials, the screw might be blocked sometimes if the temperature was too high. In this case, a fan is usually used to cool down the cold press machine keeping in a range of 98.0–112.4 °C. Because of the friction between sunflower seed shells and screw wall, the screw rotating became more difficult and generated more heat than that of SM and FSM extraction. This may wear out the screw more quickly. During the SM and FSM extraction trials, there was no screw blockages observed.

The highest oil extraction recovery was achieved at a rate of 89.74% when SM was cold pressed

at 15 Hz. For SM and FSM, the oil extraction recovery increased with the decrease of frequency of oil press machine. However, the oil extraction recovery of SS pressed at 25 Hz (74.41%) was higher than that at 20 Hz (71.92%). The processing temperature at 25 Hz, 112.4 °C, was higher than that at 20 Hz, 106.0 °C. The whole shells of SS may increase the friction at 25 Hz, which may result in a higher processing temperature at 25 Hz. This is maybe the higher processing temperature at 25 Hz caused the increased pressure, thus leading to the higher oil extraction recovery. Nevertheless, the processing temperature at 15 Hz was very close to that at 25 Hz. The smaller frequency caused the slower extrusion of oil and then led to the higher oil extraction recovery. For the extraction of SM oils and FSM oil, the processing temperatures at these three frequencies were between 98.0 °C and 100.1 °C. The small temperature difference and the relatively lower processing temperature compared with 112.4 °C did not influence the oil extraction recovery obviously. Under this situation, a smaller frequency led to a higher oil extraction recovery.

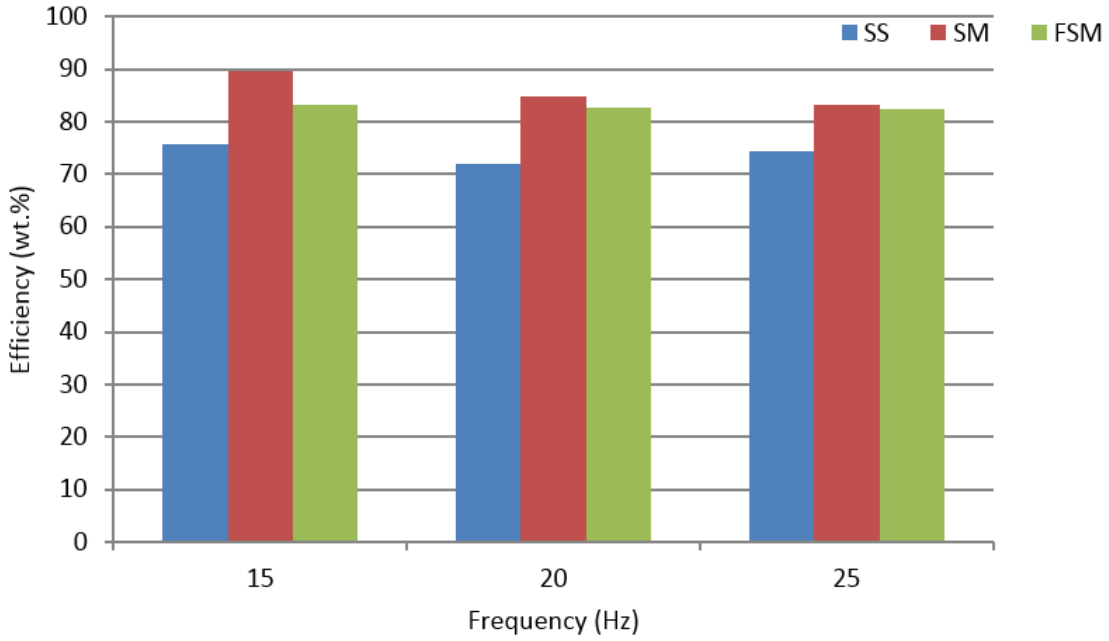


Figure 3. Efficiency (w t. %) of products obtained fr om non-food sunflow er seeds and meats.

The results show that the highest SM oil extraction recovery (89.74%) is greater than that of FSM (83.19%) and SS (75.67%). In sunflower seeds, the shells contain about 2.5% oils and the pure kernels contain about 61.25% oils [14]. That is why recovering oils from shells is more difficult than producing from pure sunflower seed kernels. A 14.07% of more sunflower oil yield would be achieved if sunflower seeds were de-hulled for oil extraction. If the profit of extra oil extraction from SM is more than the cost of de-hull processing, the pathway of sunflower oil extraction via SM is recommended. Another benefit of SM pathway is that the SM residual meal has much higher nutrient value than that of SS residual meal because the crude fibers of sunflower seed hulls have been removed. This may be extra revenue for SM pathway when the SM meal can be sold in a higher price. Due to the timeline limitation, economic evaluation of these different sunflower oil extraction pathways was not addressed in this study.

The goal of this study is to find out an effective cold press for sunflower oil extraction from SS,

SM, and FSM. Comparing sunflower oil extraction from these three feedstocks using the cold press machine at the three different frequencies, the highest oil recovery rate was obtained for all three feedstocks (SS, SM, and FSM) when the cold press ran at 15 Hz. It also was found that the cold press running frequencies have very little influence on sunflower oil properties. The cold press machine operated at 15 Hz was identified as the optimal processing parameters, therefore, the following GC-MS analysis and oil characterization would focus on the sunflower oil produced from SS, SM, and FSM using the cold press running at 15 Hz.

3.2. Chemical composition of oils

Table 2 shows the major organic compounds, volatile below 285 °C, in the sunflower oils produced by cold press at 15 Hz [28]. The sunflower oils mainly consisted of fatty acids. Fatty acid composition of vegetable oil is one of the important factors that affect vegetable oil upgrading to jet fuel. For SS oil samples, it is found that the composition of saturated fatty acids was Eicosane, Tetracosane, Octadecane, Nonacosane and Docosane, 2,21-dimethyl- in terms of relative area percentage. There were seven unsaturated fatty acids. The major unsaturated fatty acids of SS oil occupied 90.78%, while saturated fatty acids occupied 9.22%. These fatty acids varied in the extent of unsaturation and in the carbon chain length. Also, phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-ethyl-(C25:6) might be helpful to produce aromatic hydrocarbons in the future upgrading of oils for the bio-jet fuel production.

For SM oils extracted at 15 Hz, the total saturated and unsaturated fatty acid compositions were 16.78% and 83.22% respectively. The unsaturation of vegetable oils was dependent on their origin. Phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-ethyl- with an area content of 23.66% was also found in SM oils, which was a good sign for the future bio-jet fuel production.

For FSM oils cold pressed at 15 Hz, the saturate fatty acids composed 5.55% of the total fatty acids, which was Tetracosane, 1-bromo-. High free fatty acid and the water were considered to produce large amounts of soap [13].

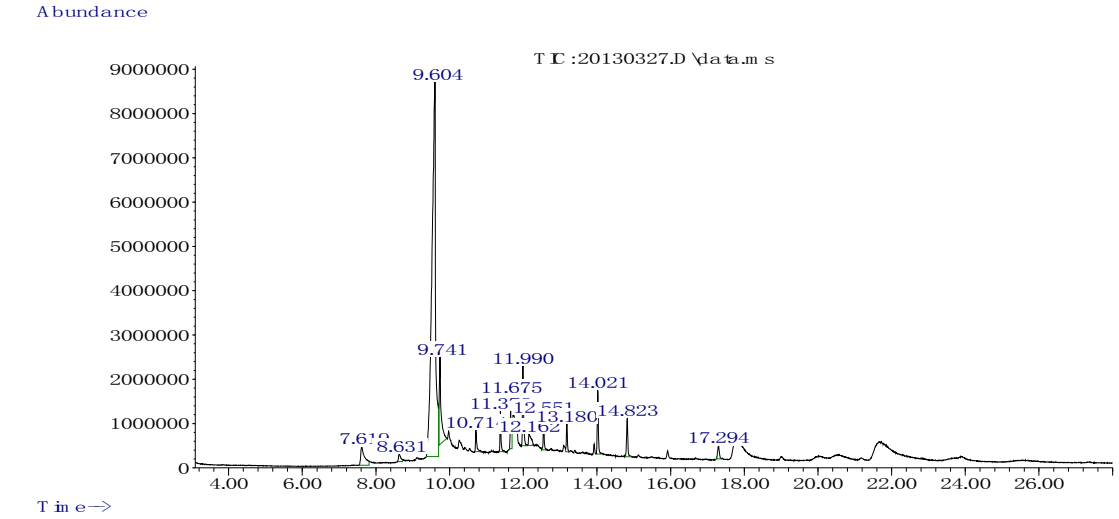
Table 2. Major components in the SS, SM, and FSM oils.

Oils	No.	Component	Retention time (min)	Area content (%)
SS	1	1-Tridecene (C13:1)	7.619	3.40
	2	Kaur-16-ene (C20:1)	8.631	0.81
	3	cis-Vaccenic acid (C18:1)	9.604	66.53
	4	Oleic Acid (C18:1)	9.741	7.10
	5	Eicosane (C20:0)	10.714	1.27
	6	Tetracosane (C24:0)	11.378	1.77
	7	13-Docosenoic acid, methyl ester, (Z)- (C23:1)	11.675	3.98
	8	Phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-ethyl-(C25:6)	11.99	4.26
	9	3-Eicosene, (E)-(C20:1)	12.162	1.46
	10	Octadecane (C18:0)	12.551	1.51
	11	Eicosane (C20:0)	13.180	1.32
	12	2,6,10,14,18,22-Tetracosahexaene, 2,6,10,15,19,23-hexamethyl-,	14.021	3.24

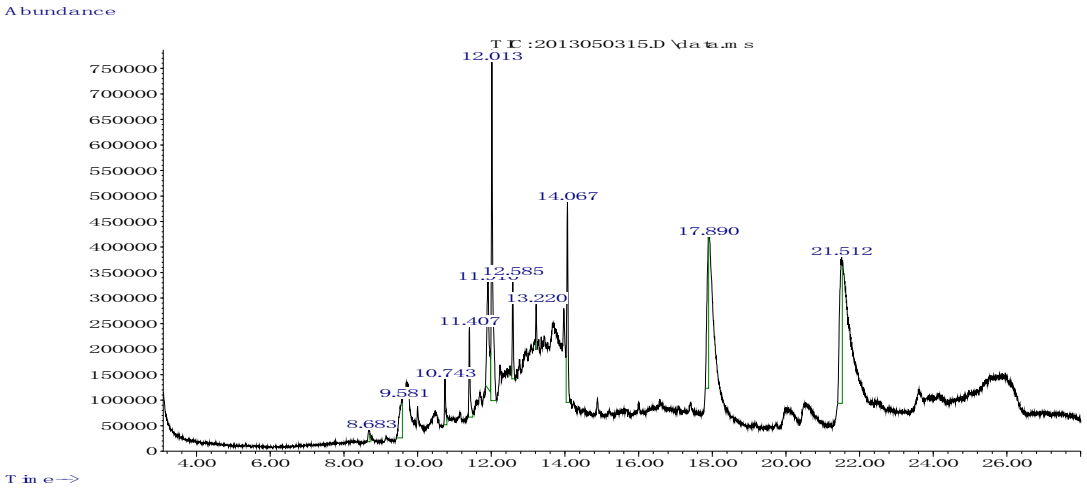
		(all-E)-(C30:6)		
	13	Nonacosane (C29:0)	14.823	2.28
	14	Docosane, 2,21-dimethyl- (C24:0)	17.294	1.07
SM	1	Bicyclopentyl-1,1'-diene (C10:2)	8.683	0.98
	2	9,12-Octadecadienoic acid (Z,Z)- (C18:2)	9.581	5.50
	3	Tricosane (C23:0)	10.743	2.65
	4	1-Nonadecene (C19:1)	11.406	5.20
	5	Oleyl alcohol, trifluoroacetate (C20:0)	11.91	12.15
	6	Phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-ethyl-(C25:6)	12.013	23.66
	7	1-Hexacosene (C26:1)	12.585	4.81
	8	Ethanol, 2-(octadecyloxy)-(C20:0)	13.22	1.97
	9	2,6,10,14,18,22-Tetracosahexaene, 2,6,10,15,19,23-hexamethyl-, (all-E)-(C30:6)	14.067	11.86
	10	Vitamin E (C29:3)	17.89	12.48
	11	17-(1,5-Dimethylhexyl)-10,13-dimethyl-4-vinylhexadecahydrocyclopenta[a]phenanthren-3-ol (C29:1)	21.512	18.73
FSM	1	cis-Z-.alpha.-Bisabolene epoxide (C15:2)	8.683	1.79
	2	cis-Vaccenic acid (C18:1)	9.553	26.06
	3	Bicyclo[10.1.0]tridec-1-ene (C13:1)	11.916	4.20
	4	Tetracosane, 1-bromo-(C24:0)	12.03	5.55
	5	2,6,10,14,18,22-Tetracosahexaene, 2,6,10,15,19,23-hexamethyl-, (all-E)-(C30:6)	14.09	7.12
	6	Vitamin E (C29:3)	17.93	39.84
	7	.gamma.-Sitosterol (C29:1)	21.546	15.43

Figure 4 represents GC-MS chromatogram and mass spectra resulted from SS, SM and FSM oils cold pressed at 15 Hz. It is obvious that the dispersion effect was good. The peak eluting at 9.604 min for SS oils was assigned to cis-Vaccenic acid. For SM oils, the peak eluting at 9.581 min was assigned to 9,12-Octadecadienoic acid (Z,Z)-. Cis-Vaccenic acid was assigned at the peak eluting of 9.553 min for FSM oils. It can be seen that the main chemical component in SS oils was C_{18}. In SM oils and FSM oils, the main chemical component was C_{25} and C_{29}, respectively. However, there was no significant difference between the large molecules in SM oils and FSM oils. The reason maybe the fact that SS have whole shells, SM have no shells, and FSM have small amounts of shell pieces. The shells mainly contain lipids and carbohydrates. In lipids, the wax is mainly composted of C_{20}. In carbohydrates, the reducing sugars are mainly pentoses, which contain five carbon atoms [35]. Some compositions from SS shells may have been introduced into the oils during the extraction process. Under this situation, SS oils contained more small molecules than that of SM oils and FSM oils. In the future research, the effect of the oil composition on the upgraded oils' yield and quality will be studied and compared.

The properties of the fatty acids, such as chain length, branching of the chain, and degree of unsaturation, could affect the bio-fuel quality [25]. The GC-MS chromatogram of oils shows that the carbon distribution lied between C_{10} and C_{30}. The carbon distribution was similar to that of diesel fuel. These oil samples contained some compositions, such as oleic acid, eicosane, tetracosane, octadecane, eicosane, 9,12-octadecadienoic acid (Z,Z)-, cis-Vaccenic acid, tetracosane, 1-bromo-, etc. These fatty acid compositions were found suitable for drop-in hydrocarbon fuel production. The free



(a)



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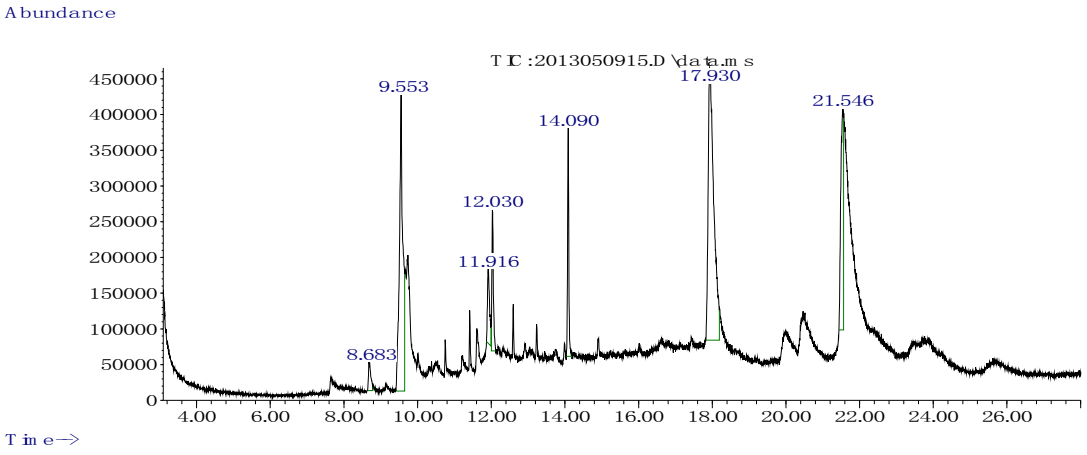

(c)

Figure 4. GC-MS chromatograms of the oil samples extracted using cold press at 15 Hz: (a) SS; (b) SM; and (c) FSM.

or bonded water in the oils will result in the formation of free fatty acids, which can corrode the engine and fuel storage tank [36,37]. In addition, free fatty acid could also be produced due to a thermal degradation. Furthermore, the content of free fatty acids is an indicator of storage conditions and the state of the raw material.

3.3. Elemental composition of oils

Table 3 represents the elemental composition of the vegetable oil samples. From Table 3, the main non-metal element of these oil samples was carbon (C), which could be up to 78.12%. The H/C molar ratios of SS oils, SM oils and FSM oils produced at 15 Hz were 1.89, 1.93 and 1.88 respectively. They were slightly lower than that of petroleum products, which is 2.0. The H/C molar ratios of SS oils, SM oils and FSM oils were similar to that of sunflower methyl ester (1.91) supplied by North Dakota State University [38]. Furthermore, all the oils had very less nitrogen content, which was less than 0.6%. The low level of nitrogen content could be related to the low level of phospholipid, thus alleviating the environmental pollution. In this case, it means that the vegetable oils have the potential for further jet fuel use. Also, the oxygen contents of these three types of oils were lower than 10.70%. The low oxygen content of the oils is attractive for the production of jet fuel.

Table 3. Elemental compositions of the oil samples.

Type of oils	Frequency (Hz)	C (%)	H (%)	N (%)	O (%)
SS	25	78.12	11.84	0.53	10.60
SS	20	77.70	11.76	0.29	10.70
SS	15	77.68	12.22	0.14	10.52
SM	25	77.80	11.80	0.17	10.36
SM	20	77.79	11.75	0.13	10.56
SM	15	77.85	12.51	0.15	10.64
FSM	25	77.22	11.64	0.46	10.54
FSM	20	77.87	11.71	0.24	10.64
FSM	15	77.32	12.11	0.24	10.20

3.4. Physical properties of oils

The pH values of oil samples produced at different frequencies are shown in Table 4. All the oils produced from sunflower seeds and meats showed a mild acidity. The pH values were not very different and they varied between 3.63 and 3.97. At related low temperature during the oil extraction machine running, mechanical aspects may have no or less effects on the pH or acidity. Since the acidity of vegetable oils reflects the content of free fatty acids which are produced from the chemical or enzymatic (lipolytic enzymes) reaction causing the split of triglycerides, mono- and diglycerides.

The density of vegetable oil produced under different frequencies is shown in Table 4. The density values show some differences, especially for SS oil sample at a frequency of 20 Hz. However, the densities of these oils were arranged between 0.869 and 0.916 g/mL, which were close to that of jet fuel (0.8 g/mL) [39]. Density is related to the chemical structure and composition. The main chemical compositions for SS, SM, and FSM oils produced at 15 Hz, as shown in Table 2, were different. This may cause the different densities between them.

The moisture content of oil samples under different frequencies is represented in Table 4. The water contents of the oil samples were very low, which were between 0.053% and 0.140%. Small amount of water left in the oil could help improve the mobility of the oil. The moisture content of Jet A/Jet A-1 was less than 0.1% [40,41]. Some moistures of produced oils may come from the feedstocks' water. Most of the water in the feedstock had been evaporated during the cold press processing due to the temperature varying between 98.0 °C and 112.4 °C. Also, some water may be left in the extruded meals. The low moisture content of these oil samples may be connected with their high viscosity, which would be stated below. Meanwhile, it also means that the vegetable oils need to be upgraded for fuel use. Furthermore, it is obvious from Table 4 that the moisture content of SS oils was higher than that of both SM and FSM oils. This is perhaps due to the hulls of the sunflower seeds containing more water that led to the higher moisture content in the oils after the cold press. The moisture contents of FSM oil samples varied from 0.053% to 0.103% under different frequencies. Maybe more water was left in the extruded meal at the faster rotating speed of screw for the small meat chips and fine hull pieces. Thus, the lower moisture content existed in the oil produced at higher frequency.

The dynamic viscosity of vegetable oil samples is shown in Table 4. The viscosity is one of the determining factors of fuel quality and uses. Also, it may significantly affect the pump and fuel injector performance in engines. The viscosity is highly dependent on the chemical structure, such as triglycerides composition, fatty acid profile, chain branching, chain length, degree of saturation and unsaturation, molecular configuration (cis-trans, conjugation), presence of degradation and oxidation products, *etc.* Compared to the dynamic viscosity of jet A/Jet A-1, 2 cP at 25 °C, the viscosities of vegetable oil samples were much higher [41]. Perhaps the large chemical molecules, such as 2, 6, 10, 14, 18, 22-Tetracosahexaene, 2, 6, 10, 15, 19, 23-hexamethyl-,(all-E)-(C30:6), and complicated molecular structures of vegetable oils resulted in the high viscosity. High viscosity fuel will not atomize properly, which may result in poor engine performance [42]. The high viscosity also indicates that the direct use of vegetable oils is impractical and the vegetable oils have to be updated before being used as bio-jet fuels.

Table 4. Physical properties of the oil samples.

Type of oils	Frequency (Hz)	pH value	Density (g/mL)	Moisture content (%)	Viscosity (cP)	Heating value (MJ/Kg)
SS	25	3.97 ± 0.014	0.874 ± 0.004	0.137 ± 0.012	75.3 ± 0.148	39.5 ± 0.003
SS	20	3.77 ± 0.146	0.916 ± 0.012	0.140 ± 0.006	77.2 ± 0.055	39.5 ± 0.003
SS	15	3.78 ± 0.001	0.879 ± 0.003	0.127 ± 0.006	76.0 ± 0.147	39.4 ± 0.003
SM	25	3.63 ± 0.025	0.884 ± 0.005	0.053 ± 0.006	72.7 ± 0.025	39.5 ± 0.007
SM	20	3.90 ± 0.017	0.887 ± 0.014	0.050 ± 0	75.0 ± 0.035	39.5 ± 0.002
SM	15	3.63 ± 0.002	0.869 ± 0.009	0.057 ± 0.006	77.3 ± 1.185	39.5 ± 0.135
FSM	25	3.49 ± 0.015	0.880 ± 0.014	0.053 ± 0.006	73.3 ± 0.025	39.4 ± 0.007
FSM	20	3.03 ± 0.040	0.889 ± 0.013	0.073 ± 0.006	76.4 ± 0.025	39.5 ± 0.030
FSM	15	3.57 ± 0.069	0.877 ± 0.019	0.103 ± 0.006	73.9 ± 0.150	39.6 ± 0.003

The heating values of oil samples are shown in Table 4. The heating values of these oil samples had no significant difference. The net heat value of Jet A or Jet A-1 was 43.2 MJ/Kg [5]. It also indicates the vegetable oils have to be updated before being used as jet fuels.

3.5. Oil content of residual meals

Table 5 lists the oil content of residual meal generated from the sunflower seeds and meats at 15 Hz. From Table 5, it could be concluded that the residual oil content of SM meal was the lowest, which was 6.14%. This states that the oil extraction recovery of SM was highest. This is maybe the hulls of SS and the few small shell particles of FSM increased the resistance to the rotating of screw, thus resulting in higher oil contents in the residual meals. This means removing the hulls of vegetable seeds could help improve the oil extraction recovery.

Table 5. Residual oil content of the sunflower meals.

Type of seeds	Residual oil content of meal (%)
SS	11.84 ± 1.280
SM	6.14 ± 0.113
FSM	10.40 ± 0.127

3.6. Preliminary tests of sunflower meat oil upgrading and distillation

Table 6 shows some properties of SM oil produced at 15 Hz and the obtained fuels after its upgrading and distillation. The undesirable properties of oils should be improved by further treatment, such as upgrading and distillation. From Table 6, there was a small increase in pH value after treatment, especially for DIF. Also, DIF and DF became lighter than SM oil. The large molecules were broken into small ones during the catalytic cracking process, which may result in the smaller density. After distillation, DF became lighter. These two properties are considered as good signs since jet A fuel has the density of 0.81 g/mL and is nonacidic [5,43,44].

Table 6. Property comparison of the SM oil, DIF, and DF from 15 Hz.

Oil/fuel	pH value	Density (g/mL)	Moisture content (%)	Viscosity (cP)	Heating value (MJ/Kg)
SM	3.63 ± 0.002	0.869 ± 0.009	0.057 ± 0.006	77.30 ± 1.185	39.5 ± 0.135
DIF	5.19 ± 0.002	0.822 ± 0.004	0.44 ± 0	5.53 ± 0.078	41.4 ± 0.053
DF	4.27 ± 0.010	0.819 ± 0.002	Undetectable	0.18 ± 0.007	42.2 ± 0.032

DIF contained more water than SM oil. There were some chemical reactions occurring during the upgrading process, and some water was produced. This may increase the moisture content of DIF. During distillation, water was evaporated. Most may be left inside the walls of tubes in the distillation system. Thus, the collected DF's moisture content was very near to zero and undetectable. Fuel's viscosity became smaller and smaller after treatment. The lower viscosity makes the fuel easier for subsequent operating and pumping. Also, fuel's heating value was higher and higher after treatment. This indicates that the upgrading and distillation treatments are effective in reconstructing the molecules. The distilled fuel has potential for future bio-jet fuel production [5,45].

4. Conclusion

The highest oil extraction recoveries for cold press of SS, SM, and FSM are 75.67%, 89.74%, and 83.19% respectively, at the frequency of 15 Hz. SM yields the highest oil extraction recovery. The cold process extraction technology is suitable for producing vegetable oils from non-food oilseed crops with high recovery.

The saturate fatty acids of SS oils produced at 15 Hz compose 9.22% of the total fatty acids. The major fatty acid is cis-Vaccenic acid. For SM oils, the content of saturated fatty acid is 16.78%. Also, 5.55% saturated fatty acids are included in FSM oils. More importantly, these three oil samples all contain suitable fatty acids for future fuel production.

The pH value, density, viscosity and heating value of oils produced at different frequencies have no significant difference. The moisture contents of the oils produced from SS are different from those of oils produced from SM and FSM since the SS feedstock contained moisture in the hulls.

For SM oil produced at 15 Hz, some properties are significantly improved after upgrading at 600 °C, such as viscosity and pH value. Also, the density dropped from 0.87 g/mL to 0.82 g/mL and the heating value increased from 39.5 MJ/Kg to 41.4 MJ/Kg. Through further treatment, DF has better properties than DIF in terms of density, moisture content, viscosity, and heating value. However, more factors, such as reaction temperature, catalyst activity, and liquid hourly space velocity, need to be considered in the future upgrading in order to meet the property requirement of bio-jet fuel derived from non-food oilseeds.

Acknowledgements

This study was funded by the U.S. Department of Transportation through NC Sun Grant Initiative under Grant No. SA0700149. The authors would like to thank the Chemical Analytic Lab in the Chemistry Department of South Dakota State University for the GC-MS analysis of the oil samples. All the supports are gratefully acknowledged. However, only the authors are responsible for the opinions expressed in this paper and for any possible error.

Conflict of interest

The authors declare that there are no conflicts of interest related to this study.

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