Production of Biodiesel from Waste Fat and Grease

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Abstract:- Processing of waste triglycerides by conventional trans-esterification is problematic due to high free fatty acid (FFA) content. Free fatty acid turns to soap that renders the trans-esterification process inoperable. Clean triglycerides such as soy, corn, and canola oils are low in FFA and easy to process but too expensive as fuel feedstocks. We have been exploring a system that combines thermal cracking of waste triglycerides with acid esterification. Middle distillates (bp 165°C-345°C) obtained by continuous thermal cracking of waste triglycerides were batch-esterified using methanol and Amberlyst 36 (wet). The yields of middle distillate from thermal cracking ranged from 58-63wt % for trap grease and 60-68 wt % for rendered animal fat. More than half of the middle distillates was fatty acids and the rest were conventional hydrocarbons. The esterification of the middle distillate with methanol was done at 90°C for 20h. Although methanol boils at 67°C, there was sufficient methanol left in the liquid phase for esterification at the elevated temperatures. This produced bio-diesel is a mixture of hydrocarbons and methyl-esters.

*Key words:-*Biodiesel, Rendered animal fat, Trap grease, Thermal cracking, Acid esterification

1. Introduction

Thermal cracking (low temperature pyrolysis) of triglycerides such as vegetable oils and fish oil was explored in the 1930s and 1940s but the availability of inexpensive crude in the subsequent decades put a damper on further developmental work [1-3]. It was only after the energy crisis in the 1970s some researchers began to investigate the production of hydrocarbons from triglycerides [4-6]. Technology development related to the use of triglycerides has been overwhelmingly in the area of trans-esterification that requires clean feeds. The high feedstock costs associated with clean triglycerides have been always problematic to the economic production of motor fuels and fuel extenders [14]. Thermal cracking of vegetable oils produced fuel with favourable characteristics such as good Cetane number and a heating value comparable to commercial diesel fuel [7,8]. Some researchers reported that simple thermal cracking of clean vegetable oils could produce fuel similar to commercial diesel fuel [8,13]. Past research also indicates that thermal cracking with or without a catalyst favored the production of naphtha over diesel fuel [1,2]. Coke formation could be a major problem during high temperature catalytic cracking [15]. It is evident from past research that the quality of pyrolysis product strongly depends on process parameters such as reaction conditions, presence or absence of a catalyst and catalyst type.

Besides clean triglycerides as mentioned above, there are low cost waste triglycerides that could be utilized in biodiesel production. Low cost rendered animal fat (RAF) is one such source. It is also referred to as 'inedible tallow and greases.' It is richer in saturates than vegetable oils. Free fatty acid (FFA) in RAF ranges from 0.5%-35% [11]. Annual production rate of RAF in the United States is about 9 kg/person/year [11]. Based on diet similarity, we expect this figure is applicable to Canada and European nations as well.

Trap grease (TPG) originates from restaurants, cafeterias and other large institutional kitchens. Trap grease is collected by a licensed cleaning company, and in North America presently it is mostly land-filled for economic reasons. Trap grease generation in the United States is about 6-8 kg/person/year [9-11]. Trap grease contains large amounts of water and solids along with FFA [11]. Groschen noted that the water content in the trap grease was uncertain but he assumed it is in the order of 60% [10]. Free fatty

acid (FFA) in TPG varies from 40% to 100% [11]. Therefore, trap grease could become a substantial source of biodiesel production, if we could develop a contaminant-tolerant processing method.

Waste triglycerides such as rendered animal fat and trap grease are problematic feeds for conventional trans-esterification. This is due to high free fatty acids concentrations (5-50%) in these oils. Normal trans-esterification uses a base catalyst such as NaOH and KOH. If FFA in triglycerides is too high, the base catalyst is consumed to form soap (saponification reaction). The soap in the reaction mixture renders the trans-esterification process inoperable. Little information exists as to how waste triglycerides such as trap grease can be converted to diesel fuels. In this paper we discuss the integration of thermal cracking of low grade waste fat and grease with the acid esterification to produce biodiesel.

2. Experimental
2.1 Feeds
Rendered animal fat (RAF) was light brown and solid at room temperature. Because it underwent a rendering process, it was 'bone dry'. Trap grease (TPG) had a sewage-like foul odour and a non-homogeneous texture. Approximately one half of collected trap grease is water [9,10]. Apparently, the trap grease used in this investigation underwent a dewatering process. It was very viscous but we could not determine the viscosity due to phase separation. Other properties are compared in Table 1. Although the physical appearances were totally different, elemental analysis indicated they were comparable.

Table 1 – Feed characteristics

Analysis	ASTM Method	Rendered animal fat	Trap grease
C, wt %	D5291-96	76.28	74.44
H, wt %	D5291-96	11.75	11.37
N, wt %	D5291-96	<0.50	0.42
S, wt %	D1552-95	0.0031	0.05
O, wt % by diff.		11.47	13.72
Ash			
H_2O, wt %	D95-83	0.06	0.59
Density at 15^oC, g/cm^3	D4052-96	0.918	0.925

Figures 1a and 1b compare thermogravimetric analysis (TGA) of rendered animal fat with that of trap grease. Preparatory tests using No. 2 diesel fuel and glycerol showed that the TGA heating rate at 50^oC resulted in weight loss curves that were close to distillation curves. Slow heating of oxygenates such as triglycerides and glycerol resulted in decomposition above 375^oC, rendering the use of TGA as a tool for simulating distillation ineffective. Accordingly all subsequent TGA were done at a heating rate of 50^oC/min. As indicated in the derivative curves, both feeds have two peaks but the peaks for TPG are significantly broader than those of RAF indicating TPG underwent considerable thermal degradation. A comparison of the TGA of trap grease with those of clean corn oil and steric acid indicated that approximately 50% of trap grease was triglycerides and the balance was degraded products, likely fatty acids such as palmitic (C_{16}) acid and steric and oleic (C_{18}) acids.

Fig. 1a – TGA of rendered animal fat
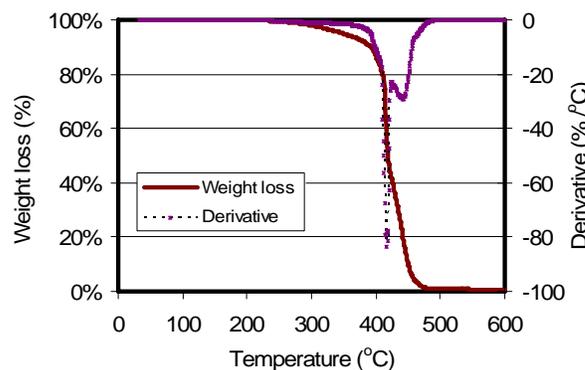
Fig. 1a – Thermogravimetric analysis of rendered animal fat
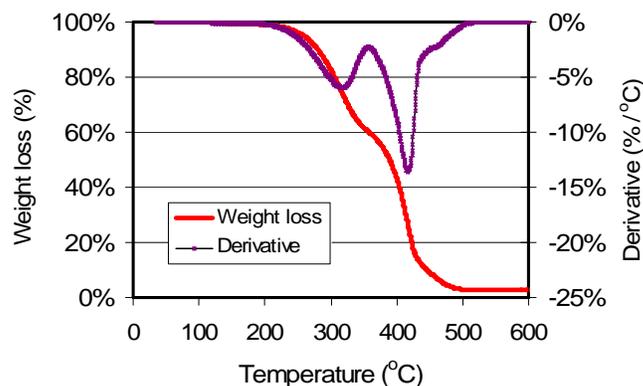
Fig. 1b – Thermogravimetric analysis of trap grease

2.2 Experimental procedures

2.2.1   Thermal cracking

Preliminary tests in a batch reactor indicated that RAF began to decompose near 350^oC and the highest gas generation occurred near 420^oC. Thermal cracking indicated by hydrocarbon generation was completed within 60 min at 420^oC. However, coke yield reached about 1 wt % (dry feed basis). Therefore, the continuous thermal cracking of RAF was done at a slightly lower cracking temperature of 410^oC and atmospheric pressure under nitrogen purge. The nominal residence was 40 min. Similarly trap grease began to decompose at 395^oC and the highest gas generation occurred near 410^oC and it continued to crack slowly at 420^oC, indicating slightly more difficult nature of TPG cracking. Thus, trap grease was cracked near 420^oC and under slight N_2 pressure (300 kPa). The nominal residence time was 40 min. Middle distillate was cut between 165^oC-345^oC in both cases.

2.2.2   Vacuum distillation

Middle distillate obtained by thermal cracking of RAF was light coloured and did not require further distillation.   However, middle distillate from thermally cracked TPG was black indicating cross contamination with residues. Before proceeding to esterification, it was vacuum distilled at 2.3 kPa to remove contaminants and lighten the colour. Upon vacuum distillation, the colour of oil improved to brownish. Approximately 13% of the initial charge remained in the vacuum still as distillation residue.

2.2.3   Acid esterification

The clean middle distillate was batch-esterified in a glass reactor with methanol using Amberlyst 36 (wet) as a solid catalyst. Fifty grams of middle distillate and 5 g of Amberlyst 36 (wet) were charged in the reactor and methanol was injected periodically using a syringe pump. Reaction temperature was kept at 90^oC and the reaction time was 20 h. As soon as methanol entered the reactor, the reaction mixture foamed. Vapour leaving the flask was condensed and passed through a dried molecular sieve 3Å in order to remove reaction water in methanol before it returned to the reactor. Because the total acid numbers (TAN) of as esterified oils were higher than the TAN specification for biodiesel, $Ca(OH)_2$ was used to neutralize unreacted FFA. Subsequently the whole product oil was centrifuged and decanted. Clear-coloured product oil was further filtered to ensure calcium soap removal from the product.

3. Results and Discussion

3.1 Mild thermal cracking

Table 2 compares thermal cracking of the two feeds under process conditions that maximized middle distillate yields. Gas analyses showed that, in both cases, the gas contained H_2, CO and CO_2 (COx) and C_1 to C_5 alkanes and alkenes. COx constituted about 70 mol% of the gas. The presence of hydrogen and COx in the reaction gas suggested the conversion of triglycerides to fatty acids and subsequent decarboxylation of fatty acids to alkanes and alkenes. Thermal cracking also produced propane and propylene along with other hydrocarbon gases. Gas from rendered animal fat registered no H_2S. This corresponds to low sulphur in the RAF feed.

Table 2 – Thermal cracking performance

Run ID	GNP040223	GNP040318
Feed		
	RAF	TPG
Thermal cracking product yields (wt %)		
Gas	1.0	1.4
Water	2.2	4.7
Naphtha	4.6	8.1
Middle distillate	67.1	63.0
Residue	25.1	22.8
Gross properties		
Water		
pH	2.01	2.64
Naphtha		
Density (g/mL)	0.783	0.776
Colour Index	1.0	7.5
Middle distillate		
Density (g/mL)	0.872	0.878
Colour Index	5.5	>8
Residue		
Coke in residue	10.7 (wt % of residue)	5 (wt % of residue)

Note 1: Naphtha is defined as IBP-165°C, middle distillate 165°C-345°C, and residue is a fraction that boils above 345°C. Note 2: Density was measured at 15°C, Note 3: Coke in residue was determined from residue TGA. Note 4: Colour index taken when liquid at 30°C.

Water produced by thermal cracking of these triglycerides was strongly acidic in both cases. The gas chromatography (GC) of naphtha indicated that it consisted mostly of light oxygenates such as propanal (CH_3CH_2CHO), acrolein (CH_2=CHCHO) acetic acid

(C_2), propanoic acid (C_3), pentanoic acid (C_5) and hexanoic acid (C_6) acids. Thus, it is likely that the strong water acidity originated mainly from simple organic acids dissolved in the water.

Table 3 summarizes naphtha characterization. Sulphur in the naphtha from RAF cracking is substantially lower than that from TG cracking. Chlorine in this fraction is high and it needs to be removed before it can be considered as gasoline supplement.

Table 3 – Naphtha characterization

Analysis	ASTM Method	RAF	TPG
		PEC040109	PEC04113
C, wt %	D5291-96	78.40	81.58
H, wt %	D5291-96	12.20	12.96
N, wt %	D5291-96	0.24	0.43
S, wt %	D1552-95	0.004	0.112
Cl, ppm		52	14
O, wt % by diff.		9.16	4.92
Viscosity at 40°C, cSt	D445-97	0.764	1.020
Density at 15°C, g/cm^3	D4052-96	0.783	0.776
Calorific value, cal/g	ISO1928	9862	10457

Figure 2 shows the TGA of middle distillate obtained from thermal cracking of TPG. It was near black and solidified at room temperature.
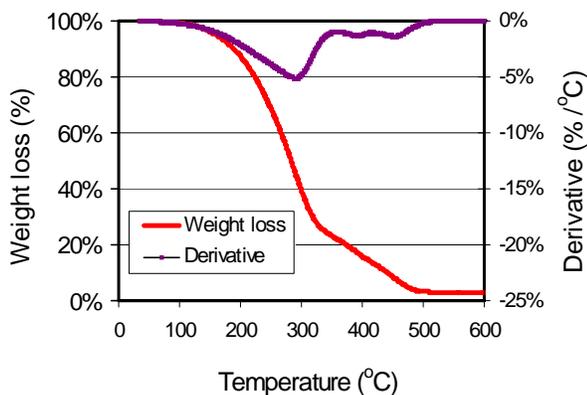
Fig. 2 – Middle distillate from TPG

As shown in Fig. 2, the middle distillate from TPG had a weight loss cure that showed two distinctive slopes before and after 320°C.

3.2 Vacuum distillation

Upon vacuum distillation, the colour of middle distillate from TPG improved to brownish. Thermogravimetric analysis of the vacuum distilled TPG middle distillate is shown in Fig. 3. It is comparable to that of RAF middle distillate. It is evident that the colour came from cross contamination by the heavy fractions that boil above 345°C.
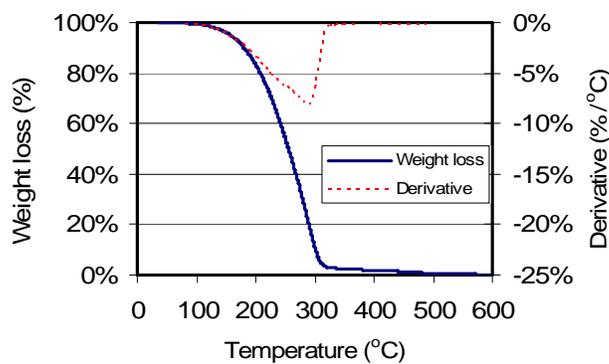
Fig. 3 – Vacuum distilled middle distillate from TPG

Table 4 compares the vacuum distilled middle distillates. Significant oxygen reduction was achieved in both cases. The acid numbers of these distillates are very high indicating controlled conversion of triglycerides to free fatty acids. The Cetane numbers of these oils are sufficiently high so that they are good candidates for diesel fuel production by further processing. Table 4 also shows that the viscosities of 'as cracked' middle distillates are still too high to be used as diesel fuel. Nitrogen in the TPG middle distillate was 0.35 wt %. This may have originated from cooking meat and fish. Likely, nitrogen in protein, under intense heat, reacted and became part of the middle distillate.

Table 5 presents the GC/MS analysis of the vacuum distilled middle distillates. It indicated that significant fraction of unsaturates such as $C_{18:1}$ (oleic acid) and $C_{18:2}$ (lin-oleic acid) degraded to lower fatty acids and others, namely hydrocarbons. Saturates such as $C_{16:0}$ (palmitic acid) and $C_{18:0}$ (stearic acid) appear more stable and retain the same carbon lengths.

Table 4 – Comparison of middle distillates

Analysis	ASTM Method	Middle distillate from RAF	Middle distillate from TPG
C, wt %	D5291-96	79.34	79.86
H, wt %	D5291-96	12.12	12.40
N, wt %	D5291-96	<0.20	0.35
S, wt %	D1552-95	<0.05	0.017
O by diff., wt %		8.29	7.37
Density (g/cm^3) at 15°C	D4052-96	0.872	0.859
Viscosity @ 40°C, cSt	D445-97	8.50	7.99
TAN, mg KOH/g	D664	146.96	121.86
Cetane number, IQT	D6890-03	59.6	54.1
Calorific value, cal/g	ISO1928	9812	9940

Table 5 – Gas chromatography/mass spectroscopy (GC/MS) of middle distillates

	Middle distillate from RAF (wt %)	Fatty acids in RAF	Middle distillate from TPG (wt %)	Fatty acids in yellow grease [11]
Fatty acids				
C$_5$-C$_{15}$ total	14.67		9.97	
C16:0	13.19	16.8	14.20	23
C16:1	1.00		1.33	1
C17:0	0.38		0.36	
C17:1	0.09		<0.01	
C18:0	5.86	8.03	4.86	10
C18:1	14.05	46.5	14.17	50
C18:2	1.07	13.5	1.09	15
C18:3	0.05	1.5	0.07	
> C20	0.31		0.51	
Grand total (wt %)	52.0	90.25	48.7	100

3.3 Acid esterification

Figure 4 compares the two final products, AVRO diesels from RAF and TPG, with conventional No. 2 diesel and soy biodiesel. AVRO diesels contain a wide variety of components and fairly well defined peaks. Two large peaks near the retention time of 8 to 9 min are methyl esters of C_{16} and $C_{18.}$ Although there are minor differences in the peak intensities, these AVRO diesels are fairly similar. Gas chromatogram peaks indicate that AVRO diesels have the characteristics of both conventional diesel and biodiesel.
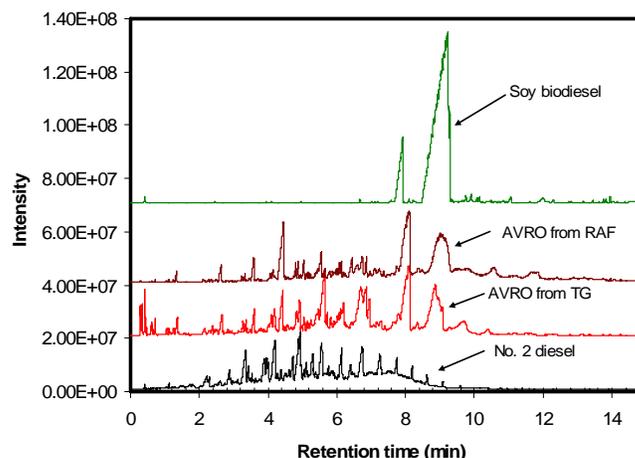
Fig. 4 - Gas chromatograms comparison of various diesel fuels

Table 6 summarizes the fuel properties of final products. Table 6 also includes the new ASTM specifications D6751-06-e1 effective May 2006 as a reference. The total acid number (TAN) of as esterified product was 2.28 mg KOH/g for RAF product and 3.36 mg KOH/g for TPG product. These products were further treated by Ca(OH)$_2$. The base treated products are identified as AVRO. Base treatment effectively reduced the total acid number to an acceptable level. Heteroatoms (S, N, Cl) in the final products are still too high. However, AVRO diesel would be blended with the regular diesel, and the heteroatom levels may be acceptable if AVRO level remains as B5 or B10 [13]. Although this particular set of data of AVRO from TPG presented in Table 6 had a high cloud point, this could be improved by cutting off a very heavy fraction by adjusting vacuum distillation temperature. When this was done, the cloud point decreased to -10°C.

Table 6 – Final products

Analysis	ASTM Method	AVRO from RAF - Ca(OH)$_2$ treated	AVRO from TPG - Ca(OH)$_2$ treated	EN14214: 2003 Spec.
C, wt %	D5291-96	79.84	80.86	
H, wt %	D5291-96	12.38	11.84	
N, wt %	D5291-96	0.016	0.22	
S, ppm	D1552-95	18	136	10
Cl, ppm	D4929-94	21	23	
O by diff., wt %		7.78	7.08	
Density (g/cm^3) at 15°C	D4052-96	0.872	0.858	0.860 ~ 0.900
Viscosity @ 40°C, cSt	D445-97	4.84	5.02	3.5 ~ 5.0
TAN, mgKOH/g	D664	0.75	0.45	0.5
Cloud point	D5773	2.4	19.1	
Pour point, ^{o}C	D5949	0.0	4.0	
Calorific value, cal/g	ISO 1928	9933	10105	
Flash point, ^{o}C	D93	115.9	130.2	Above 101

4. Conclusions

A combination of thermal cracking with acid esterification was examined for producing biodiesel from waste triglycerides. Bio-diesel produced by this method is a blend of conventional hydrocarbons and methylesters and has favourable diesel fuel properties. The approach discussed in this paper substantially expands usable feedstocks for biodiesel production. Further technical issues to be resolved are the reduction of heteroatom contents and further improvement of cold flow properties.

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