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Hydrocarbon fuel from brown grease: Effects of reaction temperature profile on yields and product distribution

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ABSTRACT

Pyrolysis of brown grease has been shown to produce kerosene-like hydrocarbons as well as ketones. The process involves several different chemical reactions of the saturated and unsaturated fatty acid components. The yields and product distributions are dependent on the reaction temperature profile, a factor that must be considered in reactor and process design. In this paper we investigated the parameters of reaction temperature and time as brown grease was preheated and held at a set of temperatures before distillation of the kerosene-like hydrocarbons. It was found that the heating and temperature profile has a significant effect on the relative yields of reaction products.

1. Introduction

The use of waste fats, oils, and greases (FOG) to prepare biofuels is of current interest because of the high costs of petroleum and disposal of unwanted oils. Biodiesel refers to the methyl esters of fatty acids, which are often blended with petroleum diesel. Green diesel refers to hydrocarbon fuels from renewable sources. Biodiesel can be produced from food-grade vegetable oils that are more expensive than diesel fuel. It is more often produced from waste cooking oil, but the demand greatly exceeds the supply, thus limiting the growth of the biodiesel industry [1]. Another potential limiting factor is the EROEI, or energy return divided by the energy invested to produce the fuel. The minimum EROEI for sustainable fuel production has been estimated as about 3:1 [2]. Required energy inputs include both production and processing of the raw materials, and for soybean and other oil crops, the energy required for production can exceed the energy cost of processing [3]. The term brown grease refers to the greasy material that collects in sewer pipes and in the sewage treatment process. In recent years, issues relating to FOG in sewer systems have intensified. In the media, sewer blockages caused by FOG waste deposits, commonly referred to as ‘fatbergs’, are becoming a reminder of the problems that FOG waste can cause when left untreated. These FOG blockages lead to sanitary sewer overflows, property flooding and contamination of water bodies with sewage [4,5]. It is generally considered a nuisance product that is often used as a low-value fuel for sludge incinerators. Brown grease consists largely of fatty acids and their calcium salts, with smaller amounts of triglycerides, and significant quantities of water and metal salts such as iron. Calcium ion leaching from concrete pipes appears to promote formation of brown grease deposits [6]. Our group reported that the chemical pyrolysis of brown grease produces a kerosene-like mixture of aliphatic hydrocarbons at between 300 and 350 °C without the use of an external catalyst [7,8]. This pyrolysis consists of several different chemical reactions, such as decarboxylation, decarbonylation, ketone formation, and probable radical reactions [9]. The same study also analyzed brown grease samples for metal ions. Many ions were present in trace amounts, but iron is the most abundant at more than 300 ppm. This is significant because the study also showed Fe(III) to promote some of the pyrolysis reactions. The high temperatures required also

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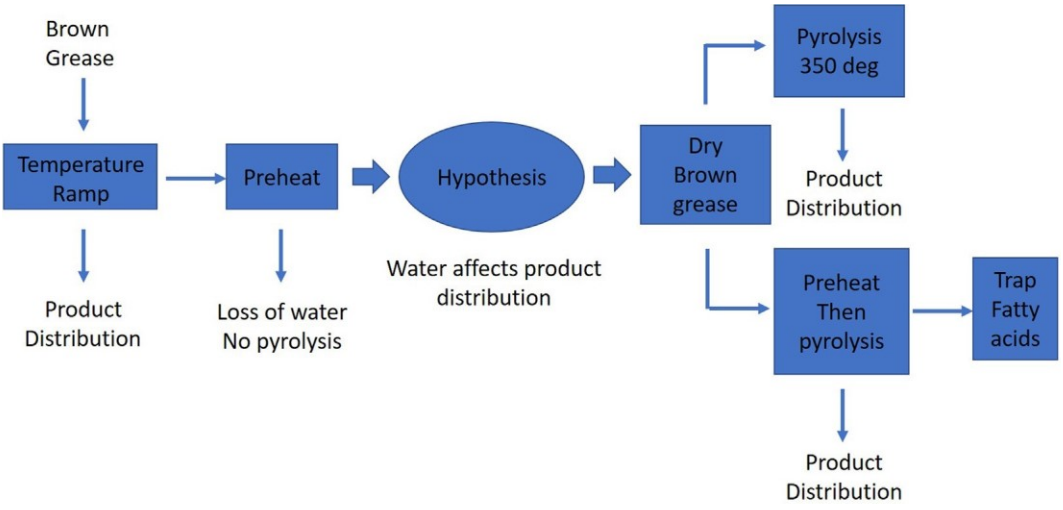

Scheme 1. Flow chart of experiments in this investigation.

kill microbes that can cause odors and possible degradation of the fuel. The potential of producing fatty acid methyl ester (FAME) biodiesel from high free fatty acid (FFA) sewage sludge components has also been demonstrated [10].

The brown grease pyrolysis was initially performed in batch mode, and the temperature was ramped up from about 100 to about 350 °C over a period of 5 h in a heating mantle, and then maintained at the higher heat setting overnight while the light hydrocarbons (< C_{18}) distilled. A heavier hydrocarbon fraction was obtained by vacuum distillation. It was assumed that the hydrocarbon forming reactions occurred at or near 350 °C, and a continuous reactor could be maintained at that temperature and the flows adjusted to obtain steady state operation. The initial attempts at a continuous reaction rapidly heated the brown grease to temperatures between 340 and 380 °C, while maintaining that temperature as fresh brown grease was added and distillate of lighter hydrocarbons collected. In each case, the reaction failed to achieve steady-state operation, as a heavy, non-volatile oil fraction accumulated in the reactor, and the rate of distillate formation decreased over time [11]. A brute force approach to distillation at higher temperatures resulted in some coke formation as well as nonvolatile oil, and reduced yields of distillate. Rerunning the batch process by setting the temperature to 350 °C immediately, instead of ramping up the temperature, also reduced the yield of volatile material and increased the formation of more non-volatile, lower value oil. Furthermore, endothermic reactions and reflux and distillation of the volatile products made it difficult to maintain the set temperature. With a set temperature of 350 °C, the actual temperatures generally ranged from about 300 to 350 °C, and could vary considerably during the reaction time.

Brown grease pyrolysis reactions take place over a range of temperatures, and these experiments showed that starting at too high a temperature reduces the yield of the most valuable hydrocarbon fraction of 17 or fewer carbon atom chains. A continuous process is more efficient than a batch process for fuels and other commodity chemicals, and a temperature ramp is more difficult to achieve in a continuous stirred tank reactor (CSTR). Pretreatment of the brown grease at a fixed temperature, followed by reactive distillation at a higher temperature is relatively simple. Thus, the goal of this project is to determine the optimum pre-treatment temperature and time for brown grease. This will enable pre-treatment to take place in one vessel, followed by transfer of the liquid to a reactive distillation apparatus, to achieve a good yield of high value distillate in the kerosene range, with minimal purge of non-volatile oil required. Fuel production from brown grease faces many of the same challenges as fuel production from petroleum. The composition of both raw materials can vary from source to source, or even within the same oil field or sewage treatment plant. Like petroleum, brown grease produces light hydrocarbons, heavy hydrocarbons, gas, and other products that may be used as heavy fuel oils or precursors for other processes. Understanding the effect of the temperature profile will enable maximum production of high value products.

2. Materials and methods

Samples of brown grease were obtained from the Torrington, CT waste water treatment plant. The oily material was separated from the water, biosolids, and debris by heating in a hot water bath and decanting the oil from the surface. All reactions were performed in a 100 mL round bottom flask with approximately 40 g of brown grease and either boiling chips or a stir bar, with boiling chips being used unless otherwise specified. The flasks were fitted with a distillation head and condenser, and the temperature was controlled by a J-kem control unit, thermocouple, and heating mantle. The parameter space consisted of pre-treatment temperature and pre-treatment time. Upon completion of each experiment, the mass of distilled water, the organic distillate (if any) and bottoms were determined by weighing, and the mass of gas produced determined by difference. The gas was presumed to be largely light hydrocarbons in addition to small amounts of CO and CO_2, and that was confirmed by flaring a sample of the reaction gas which was collected in a gas bag. The following sets of experiments are summarized graphically in Scheme 1.

A control experiment was performed in which the temperatureramp batch process was repeated, allowing a direct comparison with the experiments described below in which temperature parameters were varied. These include preheating at temperatures well below those required for pyrolysis, determination of the effect of water removal, preheating at temperatures at which some reactions have been show to occur [9], and trapping the products of that preheating.

The first set of experiments examined the effect of pre-heating the brown grease at temperatures too low to cause pyrolysis. The temperature ramp from the original batch process slowly raised the brown grease temperature through this range, so it is desirable to determine what effect, if any, it has on the product distribution. The temperature of each reaction flask was set and the time at which it reached the required temperature was recorded. Each flask was maintained at the required temperature for times ranging from one hour to 72 h. At the end of each time period, the temperature controller was set to 375 °C, but the actual flask temperature was determined by endothermic reactions and the boiling point of the distillates, generally below 350 °C. Distillation continued for 24 h, followed by analysis of both the reaction

Table 1
Percent yields of water, distillate, bottoms, and gas from temperature ramping of brown grease.

Trial	% water	% distillate	% bottoms	% gas
1	5.78	22.9	62.9	8.42
2	5.52	34.8	51.3	8.31
3	6.79	34.2	50.6	8.40

Table 2

Total percent yields (distillate plus bottoms) of light hydrocarbons, heavy hydrocarbons, fatty acids, ketones, and other compounds from temperatureramped pyrolysis of brown grease.

flask contents and distillate by GC–MS. At the conclusion of each reaction, the mass of the distilled water, organic distillate, and material remaining in the reaction flask were determined. The percent yield of water, distillate, and bottoms were recorded. From the GC peak integrations, the compounds in the distillate and reaction flasks were tabulated as percentages of light hydrocarbons (17 or fewer carbons), heavy hydrocarbons (18 or more carbons), fatty acids, ketones, and other compounds. The overall yield of each class of compound was determined from the percentage in the distillate times the yield of distillate, plus the percentage in the bottoms times the yield of bottoms.

This set of experiments was conducted in two parts. First, a quick scan was performed of the parameter space using a single experiment for each data point. That was done to determine which parts of the parameter space were most interesting, that is, if there exists a "sweet spot" that optimizes the yield of desired products while minimizing the yield of undesirable byproducts. The data consists of the overall yield of light hydrocarbons, heavy hydrocarbons, fatty acids, ketones, and the sum of the yields of light oil and fatty acids. The latter is significant because low molar mass fatty acids often co-distill with the light oil. That co-distillation can be reduced or prevented by adding a reflux zone to the distillation, which was done in the second part of this investigation.

In the second part, the interesting region of the parameter space of 225 °C from 12 to 48 h was more thoroughly examined. Each experiment was carried out in triplicate, and the mean values of the three trials were recorded. To prevent co-distillation of the low molar mass fatty acids, a Claisen adapter filled with glass beads was added between the reaction flask and distillation head, causing reflux and complete reaction of the fatty acids. The yields of water, distillate, and bottoms were determined, and the total yield of light hydrocarbons, heavy hydrocarbons, fatty acids (if any), ketones, and other compounds were determined as in the first part of this study.

A second set of experiments acted on the hypothesis that water affects the product distribution, as the brown grease samples were predried using toluene to form an azeotrope that removed the residual water. After pre-drying, pyrolysis was performed at a set temperature of 350 °C, although the actual temperature varied as described below.

A third set of experiments was performed to re-examine the effects of pre-heating, but this time, brown grease samples were heated to 300 °C for 12 h. At that temperature, degradation of unsaturated fatty acids is believed to occur, but little or no decarboxylation was observed at that temperature. To confirm the products of this initial degradation, experiments were performed in which fatty acids were trapped as their methyl esters. In the control experiment using dried but otherwise untreated brown grease, 40 g of brown grease was mixed with 32 mL methanol and 1.2 g (0.65 mL concentrated sulfuric acid), and refluxed for 4 h. The acid was neutralized with potassium carbonate and the methanol removed by distillation. The fatty acid content of the brown grease was determined by GCMS. The same procedure was used with partially reacted brown grease. Upon refluxing for 4 h. 2 poorly separated layers formed, with the upper oil layer containing most of the product. The acid was neutralized with potassium carbonate, and the methanol removed from the lower layer by distillation, and the contents of the combined layers was determined by GCMS.

The GCMS analysis was performed on a Shimadzu model QP2010S machine equipped with a Restek Rxi-5Sil MS fused silica column with a length of 30 m, inner diameter of 0.25 mm, and phase thickness of 0.25 µm. The carrier gas was helium with a flow rate of 1.2 mL/min. The column temperature profile was initial temperature 30 °C, hold for 3 min, increase to 300 at 12 °C/min, and hold for 10 min.

Trial	Light HC	Heavy HC	Fatty acids	Ketones	Other	Total
1	51.8	14.0	1.60	12.8	5.60	85.8
2	64.0	9.60	1.79	6.56	4.17	86.2
3	59.7	9.87	0.777	7.99	6.51	84.8
Average	58.5	11.2	1.39	9.10	5.43	85.6

3. Results and discussion

Our initial batch process for brown grease conversion to kerosene [7,8] was performed with a temperature ramp, and these experiments were repeated to obtain a comparison with the fixed temperature experiments. Three samples of brown grease were placed on heating mantles with boiling chips, and the temperature setting ramped from 4 (out of 10) to 7 over a period of 5 h. This corresponded to an approximate temperature range of 100–350 °C, but with the temperature variation discussed earlier due to endothermic reactions and reflux and distillation of the more volatile products. The bottoms consisted primarily of heavy hydrocarbons and ketones. The results are shown in Tables 1 and 2. This set of conditions could be approximated by a tubular flow reactor heated with a temperature gradient.

Overall, the temperature ramp experiment produced yields of light hydrocarbons in the form of alkanes and 1-alkenes in the range of C7 to C13, as well as alkanes between C14 and C17, which were accompanied by only traces of alkenes. Smaller amounts of internal alkenes were also detected. The total yield of light hydrocarbons was nearly 60%. Heavier hydrocarbons (about 11%). Ketones (about 9%), and smaller amounts of other compounds were also formed under these conditions. Although the quantity of the other compounds varies from trial to trial, it generally consists of small quantities of alcohols, esters, aldehydes, and sometimes nitrogen compounds. Water distilled early during the temperature ramp, further supporting the hypothesis, described below, that water can alter the balance between competing reactions and possibly enhance the formation of the less desirable heavy hydrocarbon and ketone products.

The next set of experiments involved pre-heating the brown grease at set temperatures for specific periods of time. These preheating temperatures started well below the temperatures needed for pyrolysis. Table 3 shows the results of the parameter space scan. The water content of the brown grease, as determined by the amount of water in the distillate, ranged from about 3.5% to upwards of 8% by mass. Brown grease is not a particularly homogenous material, and variable amounts of water remain dissolved and suspended even after decantation of the liquid FOG. The relative amounts of distillate, bottoms, and material lost as gas also varied considerably. This may be due, in part, to the difficulty of maintaining a constant temperature much above 300 °C, as will be further discussed later. Tables S-1 to S-6 in the Supporting material show the total yields (distillate plus bottoms) of light (C17 and under) hydrocarbons, heavy hydrocarbons, residual fatty acids, ketones, and other compounds. Also tabulated is the sum of light hydrocarbons and fatty acids, the latter of which can be converted to light hydrocarbons at longer reaction times. This initial set of experiments showed that light hydrocarbon and combined light hydrocarbonfatty acid yields are highest at or after 12 h of preheating, which may result in part from loss of water. No further improvement was noted after 48 h, so a more detailed study was performed at preheat times of 12, 24, and 36 h. Each of the subsequent reactions was performed in

Table 3
Yields of water, distillate, bottoms, and gases from pyrolysis of pre-heated brown grease.

Pre-heat hr	Temperature °C	% water	% distillate	% bottoms	% gas
1	225	8.55	15.09	67.96	8.40
1	250	7.99	17.46	66.35	8.19
1	275	5.77	33.79	50.93	9.50
1	300	5.31	9.92	77.84	6.92
1	325	8.03	20.05	62.58	9.34
3	225	5.72	31.48	49.34	13.45
3	250	6.20	26.97	54.80	12.03
3	275	4.15	8.55	79.41	7.90
3	300	5.21	29.12	54.82	10.85
3	325	7.24	24.52	58.80	9.43
12	225	7.70	14.88	67.43	9.99
12	250	3.81	4.20	86.43	5.56
12	275	4.27	11.69	74.28	9.76
12	300	7.36	23.36	57.15	12.13

12	325	8.09	30.25	49.33	12.33
24	225	7.97	28.24	51.04	12.76
24	250	7.89	20.19	61.80	10.13
24	275	7.06	26.96	54.81	11.16
24	300	6.27	18.74	64.19	10.80
24	325	8.08	25.56	53.78	12.58
48	225	6.61	24.89	58.71	9.78
48	250	7.67	18.08	65.84	8.42
48	275	8.20	16.74	66.03	9.03
48	300	8.06	11.88	70.59	9.47
48	325	6.33	27.11	60.49	6.06
72	225	8.61	21.17	61.98	8.24
72	250	3.56	3.04	90.39	3.01
72	275	4.97	8.48	79.73	6.81
72	300	7.22	28.12	54.90	9.75
72	325	6.96	25.33	56.25	11.46

Table 4
Yields of water, distillate, bottoms, and gas from pyrolysis of pre-heated brown grease. Each reaction is run in triplicate. Mean values are reported here, with the full Table in the Supporting material.

Pre-heat hr	Temperature °C	% water	% distillate	% bottoms	% gas
12	200	5.62	21.94	63.43	9.00
12	210	4.76	56.11	39.89	9.61
12	225	7.05	18.24	65.10	9.60
24	200	7.43	13.22	78.56	8.10
24	225	7.36	21.05	61.05	10.54
36	200	5.78	19.50	65.59	9.13
36	225	5.22	12.07	75.37	7.33

Table 5 Mean tota
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triplicate. ls of pyrolysis products with 'atty acid refl x. Each react on was

Pre-heat hr	Temperature °C	Light hydrocarbon	Heavy hydrocarbon	Fatty acids	Ketones	Other
12	200	49.0	17.8	3.4	10.8	3.8
12	210	62.2	10.1	2.1	4.6	3.7
12	225	47.7	14.7	3.5	12.0	5.3
24	200	46.7	16.3	2.2	12.5	6.9
24	225	61.7	8.0	4.8	3.9	3.6
36	200	49.7	13.4	1.8	14.4	5.8
36	225	56.8	8.6	3.0	7.2	11.8

triplicate, and results recorded in Tables 4 and 5.

The preheating temperatures in Tables 4 and 5 were too low to promote the usual brown grease pyrolysis reactions as determined by our prior study [9] and confirmed by GCMS on the bottoms after the preheating was complete. It was observed that water distilled out of the brown grease and was held up in the distillation head, thus minimizing the water reflux back into the brown grease. Upon increasing the reaction temperature, the water was able to distill out of the apparatus. This observation, as well as the lack of any brown grease reactions below 225 °C, suggested the hypothesis that water in the brown grease may be a key factor in determining the product yields. The relative yields of the reaction products varied considerably over this small temperature range. As noted earlier, maintaining a constant temperature above 300 °C for the final product forming reactions was difficult, and the difficulty may be increased by the variable water content after pre-heating. Formation of azeotropes between residual water and newly formed reaction products may also explain, in part, the variable ratios between distillate and bottoms [12]. The product distributions also varied considerably from trial to trial without a clear pattern. This may be due to the variable water content of the starting material, the variable efficiency of water removal during the preheating, and consequently, variable temperature profiles in the pyrolysis stage as residual water possibly affected the chemical reactions and formed azeotropes that altered the flask temperature during the course of the reaction.

The polarity of the fatty acids in the brown grease results in a significant ability to dissolve water. In the next set of experiments, the dissolved water was removed by an azeotropic distillation with toluene, followed by distilling off the remaining toluene. Although benzene would have been more convenient due to its lower boiling point, toluene was chosen because of its lower toxicity. It should be noted that in addition to suspended and dissolved water, some water was formed during the pyrolysis reactions, and came over with the distillate. These experiments were performed in two sets of 4 trials each. The first set was performed as the other experiments, with boiling chips added to the reaction flask but without stirring. The second set stirred the reaction flasks, likely resulting in improved heat transfer. Although the reaction flask temperature was set to 350 °C, the endothermic reactions and distillation of products from the flask caused the temperature to vary between 300 and 350 °C.

Comparison of Tables 1 and 2 with Tables 6 and 7 shows the situation to be more complex than simple pre-drying of the brown grease. Several reactions occur in the pyrolysis, and some may benefit from solvation by water, and others may suffer. For example, water has been shown to suppress ketene formation, an intermediate in ketone formation, from carboxylic acids in the gas phase [13,14]. This does not appear to occur under the current conditions, perhaps because the water and newly formed ketene are in different phases. A more important factor than aqueous solvation may be the effect of residual water, and formation of water azeotropes with reaction products, on the temperature control above 300 °C. At about 300 °C, breakdown of unsaturated fatty acids begins to occur, as was discussed in our prior work [9]. At that temperature, the reactions appear to go smoothly and the actual flask temperature remained close to the set temperature. At higher temperatures endothermic reactions occurred with release of CO and CO_2, and these often occurred in spurts, as evidenced by observation of the reaction flask and intermittent formation of CO. Thus, when the reaction temperature is set to 350 °C, the actual temperature may vary and even drop below 300 °C. Compared to the temperature ramp, pre-dried and unstirred brown grease lost more of the mass as gas products, which may include light hydrocarbons. Fewer light liquid hydrocarbons, and more heavy hydrocarbons were collected under these conditions, as well as a modest increase in ketones and other

Table 6
Percent yields of water, distillate, bottoms, and gas from pyrolysis of pre-dried brown grease. Set 1, boiling chips and no stirring, set temperature of 350 °C for 24 h.

Trial	% water	% distillate	% bottoms	% gas
1	3.38	5.93	72.8	17.9
2	4.20	4.04	74.6	17.2
3	2.27	6.17	77.8	13.7
4	5.23	5.00	73.1	16.7

Table 7
Total percent yields (distillate plus bottoms) of light hydrocarbons, heavy hydrocarbons, fatty acids, ketones, and other compounds from pyrolysis of predried brown grease. Set 1, boiling chips and no stirring, set temperature of 350 °C for 24 h.

Trial	Light HC	Heavy HC	Fatty acids	Ketones	Other	Total yield
1	33.1	20.0	0.891	17.2	7.55	78.7
2	26.9	17.8	6.70	11.1	16.1	78.6
3	28.2	18.9	7.47	12.8	16.6	84.0
4	31.0	19.1	5.47	10.6	11.9	78.1
Average	29.8	18.9	5.13	12.9	13.0	79.8

Table 8
ottoms, gas from p
Percent yieldse. Set 2, stir distillate, b nperature of 3 0°C for 24 hyrolysis of pre-dried

Trial	% water	% distillate	% bottoms	% gas

1	0.770	11.0	81.2	6.99
2	1.91	11.7	80.4	5.95
3	1.96	10.7	86.5	0.84
4	0.180	9.38	88.5	1.90

reaction products.

Stirring the reaction flask reduced the amount of material lost as gas (Table 8). It also increased the production of light hydrocarbons, as shown in Table 9, but not to the level of the temperature ramp experiments. Heavy hydrocarbon and ketone production were also modestly increased with stirring.

Two additional sets of experiments were performed to investigate the effects of pre-heating at 300 °C. At that temperature, reactions of unsaturated fatty acids begin to occur, but higher temperatures are required for extensive decomposition of fatty acids to hydrocarbons. In the first set, described by Tables 10 and 11, the stirred brown grease was maintained at 300 °C for 12 h, and then increased to a set temperature of 350 °C, resulting in actual temperatures in the 300–335 °C range. The second set was similar, except after the pre-heating at 300 °C, the residual water was removed as a toluene azeotrope, followed by a set temperature of 350 °C for 24 h, with actual temperatures in the 300–335 °C range. Those results are shown in Tables 12 and 13. In both sets, the total yield was in the 71–75% range, which included light and heavy hydrocarbons, ketones, traces of residual fatty acids, and other compounds. The light hydrocarbon fraction was similar in both cases at 51–56%, and consisted largely of pentadecane and heptadecane. Those compounds are what is expected from decarboxylation of the major saturated hydrocarbons in brown grease, hexadecanoic acid and octadecanoic acid.

Based on these results a revised hypothesis was formulated. At temperatures at or below 300 °C, mostly unsaturated fatty acids degrade into alkanes and lower molar mass carboxylic or fatty acids. Most of the other reactions occur at higher temperatures, or at around 300 °C with higher rates of heat transfer, enabling the endothermic reactions to occur more rapidly. It is at these higher temperatures that decarboxylation (single step or multi-step) and byproduct forming reactions occur. Aqueous solvation may play a role, but it appears that the major effect of water is to limit the peak reaction temperatures via reflux and distillation. This hypothesis was tested by trapping the fatty acids as their methyl esters and analysis via CGMS. With unreacted brown grease, trapping as the methyl esters showed saturated and unsaturated methyl esters in a 48.9:51.1 ratio. When the brown grease was preheated at 300 °C for 12 h, followed by trapping as the methyl esters, the product consisted primarily of methyl esters, but with some hydrocarbons and other byproducts. The product distributions from the two experiments are shown in Table 14. The product from preheated brown grease contains both saturated and unsaturated fatty esters, but the saturated esters are the major product. This includes esters of C5 to C15 acids, in addition to the major hexadecanoic and octadecanoic esters.

Table 9
Total percent yields (distillate plus bottoms) of light hydrocarbons, heavy hydrocarbons, fatty acids, ketones, and other compounds from pyrolysis of predried brown grease. Set 2, stirring, set temperature of 350 °C for 24 h.

Trial	Light HC	Heavy HC	Fatty acids	Ketones	Other	Total yield
1	37.0	24.2	1.52	20.3	9.21	92.2
2	37.5	20.4	0.699	21.8	11.7	92.1
3	33.7	22.7	7.08	16.8	17.0	97.2
4	40.4	29.5	0.561	20.5	6.92	97.9
Average	37.1	24.2	2.47	19.8	11.2	94.9

Table 10
Percent yields of water, distillate, bottoms, and gas from pyrolysis of brown grease. Heated at 300 °C for 12 h followed by 350°C for 24 h.

Trial	% water	% distillate	% bottoms	% gas
1	6.09	5.79	72.7	15.4
2	13.7	7.58	69.2	9.51
3	6.88	2.76	61.9	28.4
4	11.7	7.02	72.5	8.74

Table 11
Total percent yields (distillate plus bottoms) of light hydrocarbons, heavy hydrocarbons, fatty acids, ketones, and other compounds from pyrolysis of brown grease. Heated at 300 °C for 12 h followed by 350°C for 24 h.

Trial	Light HC	Heavy HC	Fatty acids	Ketones	Other	Total yield
1	59.8	3.74	0.389	9.13	5.49	78.5
2	56.4	8.28	0.380	7.64	4.05	76.8
3	48.3	2.60	0.132	7.77	5.87	64.7
4	40.8	12.4	0.259	16.4	9.59	79.5
Average	51.3	6.75	0.290	10.2	6.25	74.9

Table 12
Percent yields of water, distillate, bottoms, and gas from pyrolysis of brown grease. Heated at 300 °C for 12 h followed by azeotropic distillation of water with toluene, then 350°C for 24 h.

Trial	% water	% distillate	% bottoms	% gas
1	3.25	1.50	68.4	26.9
2	3.06	1.99	65.6	29.3
3	3.50	1.24	74.8	20.5
4	3.32	3.22	70.8	22.7

Table 13
Total percent yields (distillate plus bottoms) of light hydrocarbons, heavy hydrocarbons, fatty acids, ketones, and other compounds from pyrolysis of brown grease. Heated at 300 °C for 12 h followed by azeotropic distillation of water with toluene, then 350°C for 24 h.

Trial	Light HC	Heavy HC	Fatty acids	Ketones	Other	Total yield
1	57.0	5.94	0.0744	3.90	2.93	69.9
2	51.1	7.52	0.126	5.94	2.96	67.6
3	60.5	4.05	0.0413	3.94	7.51	76.0
4	54.4	7.34	0.264	8.62	3.33	74.0
Average	55.7	6.21	0.126	5.60	4.18	71.9

Table 14
Product distribution of esterification products from untreated (control) and 300 °C-preheated brown grease.

Experiment	Residual toluene	Saturated FAME	Unsaturated FAME	Hydrocarbons	Other
Control	11.5	43.3	45.2	0	0
Preheated	2.0	54.3	34.3	3.9	5.5

These results support the hypothesis that breakdown of the unsaturated fatty acids occurs at temperatures at or below 300 °C, followed by product and byproduct forming reactions at higher temperatures. The trapping of pentanoic and other low molar mass carboxylic acids proves the formation of those compounds, which would be pyrolyzed to light hydrocarbons that would be lost as gas at higher temperatures. These results also suggest a method to modulate the molar mass distribution of FAME biodiesel products from brown grease. Direct heating of dried brown grease at 350 °C forms a product rich in pentadecane and heptadecane, which is a semi-solid at room temperature. Pre-heating at lower temperatures for set times, followed by esterification, is a way to produce a better distribution of biodiesel components, with improved oxidization stability due to lower degrees of unsaturation.

4. Conclusions

Brown grease is a useful raw material for production of hydrocarbon fuels. The molar mass distribution depends on the heating profile. When the temperature is ramped up from about 100 to about 350 °C over 5 h, followed by continued heating at the higher temperature, a homologous series of alkanes and 1-alkenes is formed starting with heptane and 1heptene. Byproducts include internal alkenes, high molar mass alkenes, and ketones. Pre-heating of brown grease appears to improve the yield of more desirable light alkanes and reduce the production of ketone byproducts. This may be due, in part, to water removal.

Pyrolysis reactions at temperatures above 300 °C occur over a range of temperatures, usually below the set temperature. This is likely due to endothermic reactions and reflux and distillation of water and reaction products. Preheating at 300 °C for 12 h causes degradation of unsaturated fatty acids to lower molar mass acids and hydrocarbons, and reduces the formation of high molar mass hydrocarbon and ketone byproducts.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2018.11.053.

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