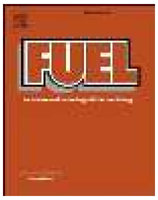
Fuel 289 (2021) 119782

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel



Full Length Article

Brown grease pyrolysis under pressure: Extending the range of reaction conditions and hydrocarbon product distributions

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ARTICLE INFO

Keywords:
Brown grease Pyrolysis
Diesel fuel Kerosene
Hydrocarbons

ABSTRACT

Pyrolysis of brown grease to hydrocarbon products was performed in a pressure reactor. Compared to our previous work at atmospheric pressure, higher reaction temperatures could be achieved. These resulted in shorter reaction times, reduced formation of undesirable ketone byproducts, and a higher percentage of the most valuable light hydrocarbon products. Higher temperatures did, however, increase the percentage of gas products at the expense of liquid products. The major liquid products are alkanes ranging from heptane to heptadecane, with smaller amounts of cycloalkanes, and in some cases, aromatic compounds.

1. Introduction

conditions [9,10].

Our previous synthesis of hydrocarbon fuels by brown grease py-

Brown grease is an abundant source of low-grade waste oil. It con- rolysis was conducted at atmospheric pressure and a set reactor temsists primarily of free fatty acids and their calcium salts, together with perature between 300 and 350 °C. Several difficulties were encountered varying amounts of triglycerides [1,2]. The compositions of brown while pyrolyzing brown grease as controlling the desired temperature is grease (BG) vary substantially depending on the source [3,4]. In addi- among the challenging tasks. Brown grease still contains some water tion to its major components, it contains numerous metal ions and even after separation, and additional water is formed during pyrolysis. volatile compounds that contribute to its sewage-like odor. The odor While water does not appear to directly interfere with the reactions, it tends to decrease over time as volatile sulfur and other compounds does reflux or distill from the reaction flask and form azeotropes with escape. Other volatile and odor causing compounds, whose composition some of the more volatile brown grease components and reaction has not been determined, co-distill with water. A rigorous study of the products or intermediates. These also reflux and/or distill from the flask, effects of those compounds has not yet been performed, but preliminary making temperature control quite difficult. It was not unusual to set the results suggest that their effects on pyrolysis are smaller at higher reactor temperature at 340 °C, and to encounter major temperature temperatures, e. g., those obtained under pressure. The high and varied fluxuations for several hours into the reaction. Part of the temperature contents of FFA makes the conversion of BG to biodiesel more chal- variation was likely from endothermic reactions, which is also seen in lenging [5,6], and yet it has been previously shown that pyrolysis of the pressure reactor, but to a much lesser extent. Attempts were also brown grease yields green diesel: hydrocarbons, primarily n-alkanes and made to determine the time required to complete the batch rection, alkenes, with some ketones and other byproducts [7]. We also had which was to be used as a first estimate of the required residence time in proposed a mechanism illustrating radical-promoted decarboxylation a continuous stirred tank reactor (CSTR). Our best estimate was between pathways [8]. Ketone and long chain hydrocarbon products are less 12 and 24 h, or when the FFA content in the reaction flask dropped valuable than the lighter hydrocarbons, as they are often solids or waxes below 1%. During the pyrolysis reactions, long chain fatty acids break at room temperature, and unsuitable for use in internal combustion down into hydrocarbons and shorter chain fatty acids. The latter are engines. Pyrolysis consists of several radical and non-radical reactions, prone to refluxing, and thus, are quite slow to react. This accounts for and the distribution of those products is dependent on the reaction the long apparent reaction times.

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Received 12 October 2020; Received in revised form 11 November 2020; Accepted 13 November 2020
0016-2361/

At atmospheric pressure, the primary product is a homologous series of straight chain hydrocarbons, with the corresponding 1-alkenes and some internal alkenes. Major byproducts are palmitone and shorter chain ketones, as well as some long chain alkanes and internal alkenes. The ketones are especially problematic as they increase the viscosity of the product oil and thus reduce its commercial potential. In contrast, the major byproducts under pressure are branched chain and cycloalkanes, aromatics, aromatics with alkyl side chains, as well as some ketones.

Pressure in the reactor is generated by gas-phase reaction products and volatile reactions and intermediates. The reactor was not pre- pressurized. The maximum pressure reached was approximately 3 MPa. Under these conditions, distillation and reflux of volatile intermediates and products was prevented, allowing the reactor to reach up to 400 °C, the maximum rated temperature of the apparatus. It also reduced the temperature changes caused by volatile material distillation and reflux. Oleic acid-brown grease biosolids mixtures have been pyrolyzed under pressure by Bressler and coworkers, but using higher temperatures and pressures than in this study [11]. Similar results were found for oleic acid pyrolysis in the presence of water [12]. In a separate study on high temperature and pressure stearic acid pyrolysis, they found a similar alkane-alkene mixture as our study with palmitic acid at atmospheric pressure, but with different product ratios [13]. The mixture of saturated and unsaturated fatty acids in brown grease has been shown to have different pyrolysis properties than pure oleic acid [9]. Furthermore, the results in this study had much lower and often undetectable FFA contents in the product compared to Bressler’s work. In contrast to their study, the brown grease in this investigation was removed from the biosolids and most of the residual water by decantation or a series of raking and screening steps. Our previous study found no advantage of retaining the biosolids in the reaction mixture during pyrolysis [7]. The pyrolysis products from brown grease are also different from those derived from palm oil waste oils and greases, even though the fatty acid content is similar [14]. This difference may be caused by numerous other substances in brown grease, some of which may inhibit desirable radical reactions.

2. Materials and methods

Brown grease samples were obtained periodically from the Torrington, Connecticut Water Pollution Control Authority. These samples were skimmed from the top of a settling tank, and contained fats, oils, and greases (FOG); biosolids, and water. The composition varies from sample to sample, but one typical sample contained about 60% by mass FOG, 25% water, and 15% biosolids. Some of the experiments were performed on a previously separated brown grease sample that was about 12 months old. This is referred to as the aged brown grease experiment. A portion of that sample was washed twice with hot water, and then toluene was added and the water and some odor-causing compounds were removed as a toluene-water azeotrope. The azeotropic distillation was repeated a second time, and the product is referred to as aged-purified brown grease. In addition, a fresh brown grease sample was collected and used within 2 months of collection. The grease was melted in a hot water bath and larger objects were removed manually. As the water and biosolids settled to the bottom, the FOG was collected from the top and used as fresh brown grease.

Reactions were performed under pressure using a Tech-Zoom 50 mL high pressure reactor. Five-gram samples of brown grease were placed in the reactor and sealed. The temperature and reaction time were set with the control unit. Upon completion, the reaction products were stored in sample vials in the freezer after taking samples for GCMS analysis.

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.

The parameter space to be explored consists of reaction time, reaction temperature, and quality of brown grease (aged, aged purified, or fresh). Initially, the parameter space was scanned and the percentage of each class of compound was estimated from the GCMS computer matches, aided by retention time and peak pattern. The classes of compound were light hydrocarbons (up to 17 carbon atoms, including cycloalkanes), heavy hydrocarbons (18 or more carbon atoms, including cycloalkanes), aromatics (hydrocarbon aromatic ring or ring system with or without aliphatic side chains), free fatty acids (FFA), and other compounds. Toluene was included in the aromatic fraction, which may be either produced from the reaction or from residual toluene from brown grease purification or cleaning of the reactor. After the initial parameter space scan, the most interesting regions were re-examined by running the reactions in triplicate and determination of the reaction yield.

3. Results and discussion

Our prior work determined that below 310 °C, the pyrolysis reactions do not occur at an appreciable rate. The product distributions at 310 °C for 24 h was compared for the 3 brown grease samples: Aged (aged 12 months without additional purification), aged purified (aged 12 months, purified by water washing and azeotropic distillation with toluene), and fresh (decanted from water and solids). Fresh brown grease contains odor causing compounds, likely containing sulfur, nitrogen, or both. Being rather volatile, the amount of those compounds is likely to decline over time in brown grease.

Table 1 shows the relative amounts of products. At 310 °C, few aromatic compounds were formed. In the aged samples, about 40% of hydrocarbons are formed, although a good amount of free fatty acid was unreacted. In fresh samples, about 28% of hydrocarbons are observed with a larger quantity of ketones. After 24 h the pyrolysis at 310 °C didn’t go to completion as illustrated by the large percentage of unreacted fatty acids. The long required reaction time at this temperature, and the apparent sensitivity to small changes in brown grease composition, are disadvantageous of brown grease pyrolysis at this low temperature. A possible advantage is when a low percentage of aromatic compounds is desired, although a higher temperature will still be required to make this transformation commercially viable.

The pyrolysis reactions were performed at 325 °C for 24 h, as shown in Table 2. Compared to the previous set, the aromatic content of the products was slightly higher. Unlike at 315 °C, the reactions at 325 °C had improved conversion of free fatty acids. The products distributions of the three samples are comparable. A separate experiment showed the reaction to be incomplete after 12 h. In our prior study [10], the actual reaction temperature at atmospheric pressure was in the vicinity of 325 °C, but refluxing and distillation of the more volatile reactants, products, intermediates, water, and numerous azeotropes caused major variations in temperature during the course of the reaction, and required residence times were difficult to determine. These problems were avoided by running the reaction under pressure.

The next set of experiments increased the reaction temperature to 350 °C for reaction times of 12 and 24 h. Over all, twelve hours was sufficient to complete the reaction, as seen by the low or undetectable

Table 1
Product distribution percentage from brown grease pyrolysis at 310 °C.

Experiment	Rxn. Time (hrs)	Lt HC	Hv HC	Aromatic	FFA	Ketones	Other
Aged	24	33.4	6.4	0.4	32.4	27.0	0.4
Aged purified	24	31.9	6.8	1.9	22.5	33.8	3.1
Fresh	24	15.9	11.8	0.0	31.4	37.7	3.3

Lt HC: light hydrocarbons; hv HC: heavy hydrocarbon; Aromatic: Aromatic hydrocarbons w/ or w/o aliphatic side chain; FFA: free fatty acids

Table 2
Product distribution percentage from brown grease pyrolysis at 325 °C.

Experiment	Rxn. Time (hrs)	Lt HC	Hv HC	Aromatic	FFA	Ketones	Other
Aged	24	48.0	8.9	1.0	0	41.7	0.5
Aged purified	24	46.8	8.2	4.1	1.8	38.6	0.5

Fresh	24	50.4	9.2	0	9.3	31.1	0

levels of FFA in each of the product mixtures. At 350 °C, the differences in product distribution between the aged, aged-purified, and fresh samples were rather small, and may be primarily due to random variation between samples. This suggests little advantage of ageing the brown grease or using it immediately after production, nor is there much to be gained by a pre-purification process.

Table 4 shows the product distribution at 375 °C. The reactions were completed at 12 h at this temperature. Aged samples provided about 86% of hydrocarbons, a smaller amount of ketones compared to other conditions conducted in the experiments. The percentages of hydrocarbons from the aged, aged-purified, and fresh samples are comparable for each of the three reaction times. The largest differences in product distribution was at 3 h, where the reaction had not yet reached completion, and more unreacted FFA was present with the fresh grown grease. Those differences were minimized by 6 h when the reaction was largely complete.

Analysis of this scan of the parameter space revealed some interesting trends. Of all the reaction products or byproducts, the light hydrocarbon fraction is economically the most valuable, being largely in the boiling range of straight run gasoline, kerosene, and diesel fuels. Diesel fuel can contain up to 35% aromatics, although lower aromatic contents can be desirable as they produce less soot. High FFA content fuels will damage engines by excessive corrosion. FFA removal is relatively simple, but it wastes (or at least causes the need to recycle) starting material. Thus, minimizing the FFA content in the product reduces production costs. Most of the ketone byproducts are of sufficiently high molar mass as to solidify at room temperature, although lower molar mass ketones may be beneficial as they partially oxygenate the fuel, thus reducing hydrocarbon and CO pollution. Minimization of the high boiling components makes it easier to purify the product by distillation.

Comparison of Tables 1-4 shows that higher temperatures both maximize light hydrocarbon formation and minimize FFA and ketone production. They also result in significantly shorter reaction times, which minimizes production costs in both a batch and continuous reactor system. Aromatics are formed at 375 °C, but at levels far below the maximum for commercial diesel fuel. Aromatics, cycloalkanes, and branched alkanes are also components of gasoline. Thus, the reactions were revisited at 375 and 400 °C, the latter being the highest rated temperature for this reactor. In this next set, only fresh brown grease was used as there appears to be no advantage to ageing the grease prior to use; and each reaction was performed in triplicate to minimize false trends due to random variation between trials.

Table 3

Product distribution percentage from brown grease pyrolysis at 350 °C.

Experiment	Rxn. Time (hrs)	Lt HC	Hv HC	Aromatic	FFA	Ketones	Other
Aged	24	74.9	6.4	0.9	0	16.8	1.0
Aged purified	24	69.6	7.3	2.6	0	20.2	0.5
Fresh	24	71.9	10.0	0	0	15.6	2.6
Aged	12	63.7	9.6	0	0	26.0	0.8
Aged purified	12	61.7	8.5	2.5	0.8	25.7	0.9
Fresh	12	65.7	7.3	0.5	0.8	22.6	3.1

Table 4

Product distribution percentage from brown grease pyrolysis at 375 °C.

Experiment	Rxn. Time (hrs)	Lt HC	Hv HC	Aromatic	FFA	Ketones	Other
Aged	12	77.8	7.9	1.1	0	12.6	0.5
Aged purified	12	73.6	6.5	3.4	0	15.1	1.5
fresh	12	74.6	8.9	1.1	0.9	8.6	5.9
Aged	6	71.4	5.9	1.1	1.0	18.8	1.8
Aged purified	6	70.5	8.4	2.7	3.4	13.5	1.5
Fresh	6	69.2	4.9	1.3	4.2	18.6	1.9
Aged	3	61.6	6.7	0	9.7	21.5	0.5
Aged purified	3	61.0	5.4	3.3	8.7	21.0	0.6
Fresh	3	60.4	2.7	0.64	20.4	12.8	3.1

The data in Table 5 shows the product composition from reaction at 375 °C and the percent yield of liquid product. The remainder of the mass was lost as gas, along with small quantities of suspended solids. Comparison of the 4 h and 6 h reaction times show similar product distributions, except for lower FFA content at 6 h, indicating higher conversion of starting material. The higher conversion was offset by a lower yield of liquid fraction, although the gas fraction is still likely a valuable commercial product. In each case, the total aliphatic hydrocarbon content exceeded 70% of the liquid fraction.

The brown grease reaction at 400 °C resulted in faster reaction completion times and lower ketone content, but with a larger fraction of material converted to gas. Prior work showed this gas contains CO and CO_2, and from flaring experiments, it likely also contains light hydrocarbons. The results are summarized in Table 6. The high FFA content indicates that the reaction is incomplete after one hour, but essentially complete after 4 h. In general, higher ketone contents were favored by lower temperatures, which explains the high ketone contents in our prior work at atmospheric pressure. Under the current conditions, it takes about 2 h for the reactor to heat up to operating temperature, and another 2–3 h to cool down. It is likely that significant amounts of ketones are formed during the initial heating period, particular for the reactions run at the higher end of the temperature range. This suggests that a continuous rector may produce an even lower ketone content after a ketone-rich forerun. That possibility will be investigated in the near future.

An additional experiment was performed to determine the effect of high temperatures on ketone byproducts that were already formed in the reaction. For this experiment, the "bottoms" fraction from some prior experiments was heated to 375 °C for 6 h, and the GCMS of the sample before and after this additional pyrolysis were compared, as shown in Fig. 1. Initially, this bottoms fraction contained large amounts of pentadecane, heptadecane, ketones, FFA, and smaller amounts of other reaction products. After 6 h under pressure at 375 °C, most of the ketones and all of the remaining fatty acids were converted to hydrocarbon products. Furthermore, there was significant equilibration among the initial alkane products, with extensive formation of alkanes in the C7 to C14 range. Coke was also formed in this reaction, analogous to coking reactions of heavy petroleum fractions to produce coke and lighter hydrocarbons. Thus, this

Table 5

Product distribution percentage from brown grease pyrolysis at 375 °C as a function of reaction time.

Time (hrs)	Lt HC	Hv HC	Aromatic	FFA	Ketones	Other	% liquid
4 T-1	67.6	4.8	0	6.4	19.0	2.1	77.3
4 T-2	66.8	5.6	1.2	7.0	19.4	0	79.3
4 T-3	66.8	8.2	0	0	23.9	1.1	73.3
4 Ave.	**67.1**	**6.2**	**0.41**	**4.5**	**20.8**	**1.1**	**76.6**
6 T-1	68.4	6.6	0.5	0	21.6	2.9	64.5
6 T-2	65.3	6.2	7.1	0	19.4	2.0	72.3
6 T-3	65.3	6.7	0.5	3.0	21.4	3.1	64.0
6 Ave.	**66.3**	**6.5**	**2.7**	**1.0**	**20.8**	**2.7**	**66.9**

Table 6

Product distribution percentage from brown grease pyrolysis at 400 °C as a function of reaction time.

Time (hrs)	Lt HC	Hv HC	Aromatic	FFA	Ketones	Other	% liquid
1 T-1	66.9	4.7	0.6	14.3	7.7	5.8	59.6
1 T-2	67.0	2.4	2.6	15.3	6.4	6.3	67.6
1 T-3	73.8	5.5	1.0	2.5	15.9	1.3	75.6
1 Ave.	**69.2**	**4.2**	**1.4**	**10.7**	**10.0**	**4.5**	**67.6**
4 T-1	83.2	3.9	3.5	1.2	6.1	2.0	45.4
4 T-2	78.9	2.7	5.3	0	13.2	0	52.4
4 T-3	81.3	3.2	3.2	0	10.4	2.0	48.0
4 Ave.	**81.1**	**3.3**	**4.0**	**0.4**	**9.9**	**1.3**	**48.6**

coking of brown grease heavy oil products can be used to enhance the yield of desirable light hydrocarbon products, as illustrated in Table 7.

4. Safety concerns

The reactions described here produce flammable hydrocarbons and a gas containing hydrocarbons and CO.

5. Conclusions

Brown grease pyrolysis in a pressure reactor has several advantages compared to reactions under atmospheric pressure. First, times to completion are more easily estimated under pressure because the reflux and distillation of volatile reactants, products, intermediates, and azeotropes is avoided. Higher temperatures can also be achieved, resulting in shorter reaction times and fewer ketone byproducts, which cause the product to solidify at lower temperatures. At the higher temperatures, larger quantities of the more volatile light hydrocarbons are formed in the liquid phase, but higher temperatures also reduces the total amount of liquid formed. However, the gas fraction is still likely to be useful as a fuel. Under all conditions examined, there is some trial to trial variation in the product distribution, but that variation is minimized at higher temperatures. Under the optimum rection conditions, there is relatively little difference in the products from fresh or aged brown grease, and there is little advantage in using a pre-purification process to remove water and odor-causing compounds. Although the optimal pyrolysis conditions do not completely eliminate the heavy, less desirable reaction byproducts, those can be degraded by coking to higher value products.

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CRediT authorship contribution statement

Lawrence M. Pratt: Conceptualization, Funding acquisition, Investigation, Methodology, Writing original draft, Writing editing. **Jihyun Kim:** Data curation, Formal analysis. **Ho-Yin Lo:** Resources, Data curation. **Dequan Xiao:** Conceptualization.

Table 7
Composition of brown grease pyrolysis “bottoms” before and after coking.

Composition	Lt HC	Hv HC	Aromatic	FFA	Ketones	Other
Before	34.2	22.1	0	27.2	13.5	3.0
After	70.1	15.5	1.5	0	7.9	5.0

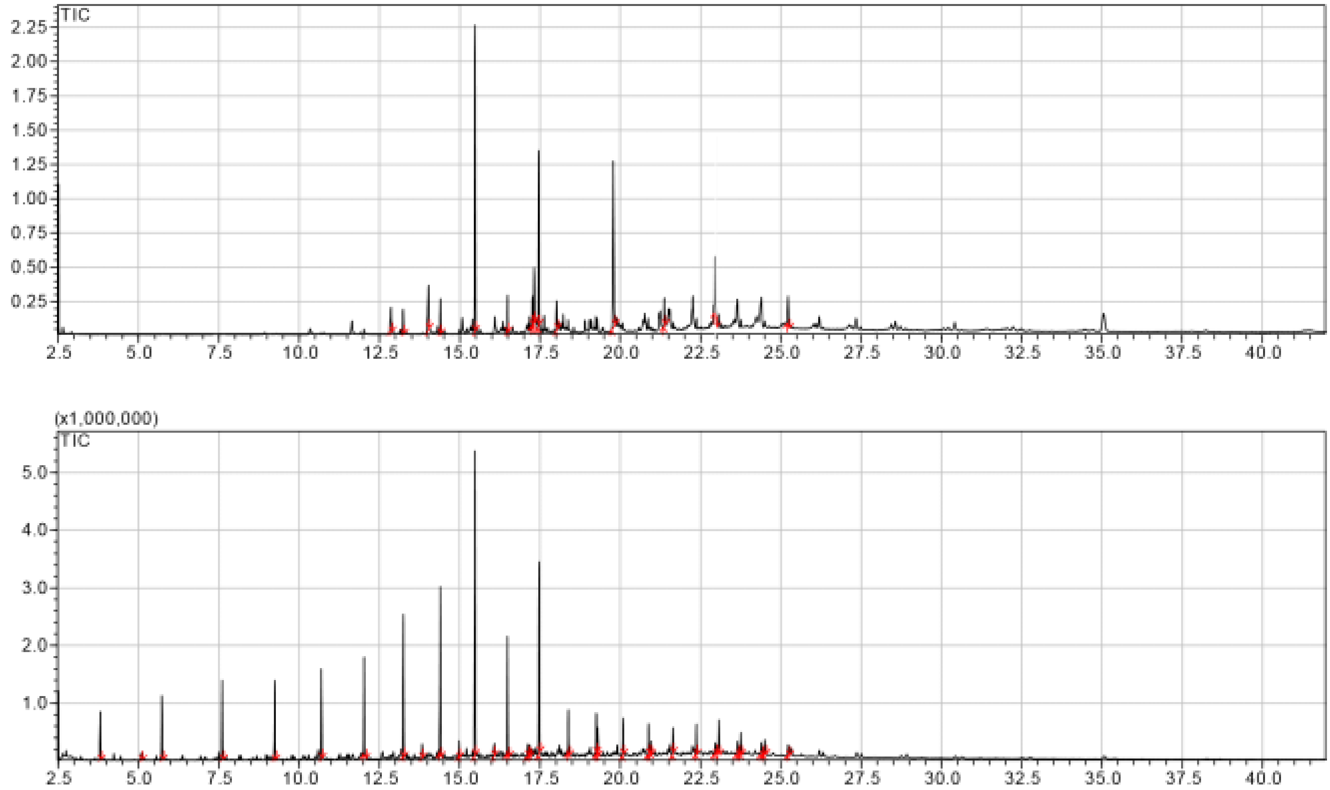

Fig. 1. Bottoms fraction from prior pyrolysis of brown grease at atmospheric pressure. Top: Bottoms before coking at 375 °C; Bottom: After coking at 375 °C under pressure for 6 h.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

This work was supported in part by NSF grant #CBET 1802524 (LP), and by the Jacob Buckman Chair Fund (DX).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2020.119782.

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