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Desulphurization of drop-in fuel produced through lipid pyrolysis using brown grease and biosolids feedstocks / Bartoli, Mattia; Asomaning, Justice; Xia, Lin; Chae, Michael; Bressler, David C.. - In: BIOMASS & BIOENERGY. - ISSN 0961-9534. - ELETTRONICO. - 154:(2021), p. 106233. [10.1016/j.biombioe.2021.106233]

Availability:

This version is available at: 11583/2924966 since: 2021-09-19T18:50:49Z

Publisher:

Elsevier

Published

DOI:10.1016/j.biombioe.2021.106233

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Desulphurization of drop-in fuel produced through lipid pyrolysis using brown grease and biosolids feedstocks

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ARTICLE INFO

Keywords:

Biofuel
Fatty acids
Biosolids
Pyrolysis
Desulphurization

ABSTRACT

Biosolids can be incorporated as a water replacement into a two-stage thermal process for biofuel production from brown greases, significantly reducing the overall environmental impact of the process. Unfortunately, the use of biosolids resulted in an appreciable amount of sulphur in the pyrolytic oils produced in the final stage of the process. Here, we first evaluated the relationship between the sulphur content of fatty acids pyrolysis liquid products and pyrolytic conditions. Afterwards, we evaluated the sulphur removal efficiency of several approaches such as distillation, extraction and adsorption. Through a combination of distillation and liquid-liquid extraction, we achieved a desulphurization of up to 95% reaching a final sulphur concentration of 15 ± 4 ppm.

1. Introduction

There is a finite supply of crude oil in the world [1], yet the demand for raw materials and fuels from the fossil fuel industry is growing every year, especially in the developing world [2]. As a consequence, research into renewable resources that are able to supply alternatives to oil has become very attractive [3]. Biomass is a very promising source to satisfy the growing requirement for energy and raw materials and additionally offers benefits in the reduction of environmental impact [4]. The main issue regarding the use of lignocellulosic biomass is the high oxygen content of the composite fractions [5], but the use of feedstocks such as fatty acids found in algae [6,7] as well as inedible fats and oils [8] could solve this issue. These raw materials have received a remarkable amount of attention with regards to biodiesel production through transesterification to obtain ester derivatives [9].

An alternative route for the conversion of fatty acids into biofuel is based on thermal cracking during a pyrolytic process [10,11]. Asomaning et al. [12] reported a two-stage lipid pyrolysis process that uses fatty acids recovered from hydrolysis of inedible fats as feedstock for a pyrolysis conversion into renewable drop-in fuels. A recent development in this process was the incorporation of biosolids as a replacement for water during the hydrolysis step [13]. Biosolids can contain a high amount of sulphur (up to 600–1000 ppm) as well as inorganic (35 wt% of solid residue) and organic (65 wt% of solid residue) compounds [14]. The high sulphur content of biosolids can negatively affect the quality of the resulting pyrolysis product, as sulphur levels are tightly regulated in

transportation fuels [15,16]. Omidghane et al. [13] demonstrated that significant levels of sulphur are carried over into the liquid pyrolysis product generated from fatty acids derived from brown grease hydrolyzed with biosolids. Thus, incorporation of biosolids into lipid pyrolysis may require the development of methods to reduce sulphur levels in the liquid pyrolysis product.

Sulphur removal is a common practice in traditional oil refinery processes [17] and several methodologies have been developed [18], but hydrodesulphurization is currently the most used technique [19–22]. Hydrodesulphurization converts sulphur species into H_2S , which can be easily removed, though this procedure requires high temperatures, high H_2 pressure [23,24], and the mandatory use of a catalytic system [25]. Possible alternatives to hydrodesulphurization are oxidative desulphurization and/or adsorption.

Oxidative desulphurization converts water insoluble, low-oxidation state sulphur species into hydrosoluble ones (*i.e.* sulfones), which is followed by an extraction in water [26] or in ionic liquids [27]. This method can be performed using electromagnetic irradiation [28,29], ultrasound [30] or electrochemical [31] techniques with several oxidants and metal catalytic systems [32–35]. Alternatively, adsorption has been applied to decrease sulphur content in diesel fuels using zeolites [36,37], activated carbon [38,39], aluminosilicates [40,41], or modified materials containing ZnO and Ni as in the case of reactive adsorption [42]. As reported by Srivastava [18], the use of adsorbents to remove sulphur compounds from hydrocarbon mixtures can be problematic as aromatic compounds readily interact with common adsorbents such as

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Table 1

Properties of adsorbents. Values are as provided by the manufacturers of the adsorbent in the specification and materials data.

Adsorbent	Functional group	Particle size (μm)	Surface area (m^2/g)
Activated carbon	n.a	≤ 5000	600–800
Microcrystalline cellulose	n.a	50	20
Dowex marathon M5A6	Sulphonic acid	600–750	28
Dowex 66	Tertiary amine	300–1200	33
Amberlite IRC86	Carboxylic acid	500–700	35
Amberlite IR400	Quaternary amine	600–750	33
Amberlite IR66	Sulphonic acid	300–1100	28
Amberlyst A21	Tertiary amine	490–690	34
Silica	n.a	37–60	400
Kaolin	n.a	0.2–0.6	22
Celite	n.a	≤ 300	~ 1

Note: n.a = information/data not available.

activated carbon, inorganic porous materials, and styrenic/divinyl benzene-based resins. Aromatics are a very important class of compounds in liquid fuels and thus, their removal from the crude pyrolysis product is undesirable. Furthermore, the regeneration of the adsorbents through washing cycles and chemical treatments could drastically increase the environmental impact of this technology.

This work explores the effects of pyrolysis on desulphurization of the fatty acid-enriched organic fraction recovered after brown grease was hydrolyzed using biosolids as a water replacement at a weight ratio of 1:1. The influence of temperature and process time were studied in 15 mL batch microreactors. A comparison between the results obtained with the 15 mL microreactors and a 1 L mechanically stirred batch reactor was also investigated. After establishing a correlation between pyrolytic conditions and sulphur content, we carefully evaluated desulphurization approaches based on extraction, distillation, and selective adsorption of sulphur-containing species. These approaches do not consume reagents such as hydrogen in hydrodesulphurization or oxidative agents in oxidative desulphurization while preserving the aromatic fractions. Furthermore, these approaches could be easily combined to improve desulphurization, resulting in a product that meets stringent sulphur content regulations for automotive fuels.

2. Materials and methods

2.1. Materials

The fatty acids derived from the hydrolysis of brown grease with biosolids that were used as feedstock in the pyrolysis experiments in this study were the subject of another study where detailed experimental processes and conditions as well as product composition and quality are reported [43]. Going forward, “fatty acids derived from the hydrolysis of brown grease with biosolids” will be referred to as “fatty acids feedstock” for simplicity and clarity. Pentane (HPLC grade, >99.9%), hexane (HPLC grade, >99.9%), and the internal standard (methyl nonadecanoate; $\geq 98.0\%$) for gas chromatography (GC) of the liquid products were purchased from Sigma-Aldrich (St. Louis, MO, USA). Diazald (N-methyl-N-nitroso-p-toluenesulfonamide; TLC PharmaChem Inc (Concord, ON, Canada)) was processed using a Diazald kit from Sigma-Aldrich (St. Louis, MO, USA) to produce diazomethane, which was then used to derivatize fatty acids. Activated carbon was purchased from Sigma Aldrich (Netherlands) and microcrystalline cellulose was purchased from Sigma Aldrich (Ireland). Potassium hydroxide (99%), hydrochloric acid (37%), Dowex Marathon M5A6, Dowex 66, Amberlite IRC86, Amberlite IR400, Amberlite IR66, Amberlyst A21, and acetic acid (98%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Silica was purchased from Fisher Scientific (Fair Lawn, NJ, USA), Celite

was purchased from Megazyme (Bray, Ireland), and kaolin was purchased from KaMin (Macon, GA, USA). Activated carbon, microcrystalline cellulose, Dowex Marathon M5A6, Dowex 66, Amberlite IRC86, Amberlite IR400, Amberlite IR66, Amberlyst A21, kaolin, celite and silica were used as received without modifications as adsorbent materials for the desulphurization procedures. The properties of these adsorbents are reported in Table 1. Air, N_2 , H_2 , and He gases were purchased from Praxair (Praxair Inc., Edmonton, AB, Canada).

2.2. Methods

2.2.1. Pyrolysis experimental procedure

Pyrolysis reactions were initially conducted in 15 mL batch microreactors made from $\frac{3}{4}$ inch stainless steel Swagelok (Edmonton, AB) fittings and tubing as described by Asomaning et al. [44] at 410, 430 and 450 °C for reaction time up to 3 h.

A second set of pyrolysis reactions was conducted in a 1 L batch reactor (Parr Instrument Co., Moline, IL) heated by an electric heating element located outside of the reactor vessel as described elsewhere [12]. Thermocouples enabled real-time measurements of the internal reactor temperature and pressure transducers allowed measurement of the internal reactor pressure. Each reaction was conducted by loading approximately 100 g of the fatty acids feedstock into the reactor vessel. The reactor was checked for leaks and then purged with nitrogen at 500 psi. The heater and stirrer (200 rpm) were then turned on. Reactions were carried out at 410, 430 or 450 °C for 1 h after the set temperature was reached (thermal steady state reached in 1.5 h). At the end of the reaction, the heater was stopped, and the heating mantle was removed from the reactor vessel to allow cooling. Fractions were recovered according to procedures previously reported [12].

2.2.2. Distillation of crude pyrolysis product

15 mL of crude pyrolysis product obtained from pyrolysis at 410 °C using the 1 L reactor were distilled at atmospheric pressure using an Aldrich® distillation head purchased by Sigma Aldrich (St. Louis, MO, USA). Two distilled fractions collected in the temperature range between room temperature to 100 °C, or from 100 °C to 200 °C, as well as the undistilled residue, were recovered, weighted, and analyzed.

2.2.3. Extraction procedures

Solid-liquid extractions of sulphur compounds from the feedstock were performed using two different approaches. In the first approach, 5 g of the fatty acids feedstock was put into a glass tube preloaded with 0.5 g of adsorbent being tested (i.e. activated carbon, silica, kaolin, Celite, or microcrystalline cellulose). 5 mL of water and 5 mL of 6 M KOH were then added. The slurry was stirred at room temperature for 3 h. Afterwards, 37% HCl was added dropwise until a pH of 2–3 was reached, which was determined using colorpHast indicator strips (Fisher Scientific; Fair Lawn, NJ, USA). The biphasic solution was centrifuged at $7155 \times g$ for 10 min, after which the upper liquid phase was separated by decanting.

The second approach involved extracting 5 g of the fatty acids feedstock for 3 h using a Soxhlet extractor with a cartridge pre-filled with 5 g of the adsorbent being tested using 100 mL of distilled water. After the extraction, the upper organic phase was recovered and characterized. The adsorbent was also recovered by centrifugation of the water phase at $7155 \times g$ for 5 min, and was then dried for 16 h at 80 °C. This procedure allows the extraction of low boiling sulphur compounds without adversely affecting the concentration of valuable compounds that could be retained on the surface of the adsorbents.

For liquid-liquid extractions, 15 g of crude liquid pyrolysis product from the 1 L scaled-up pyrolysis experiments at 410 °C was put in a separatory funnel with 10 mL of 6 M KOH (pH 12–13) and 100 mL of water. After phase separation was complete, the upper organic phase was recovered and characterized through chromatographic analysis. The bottom aqueous phase was put into another separatory funnel and

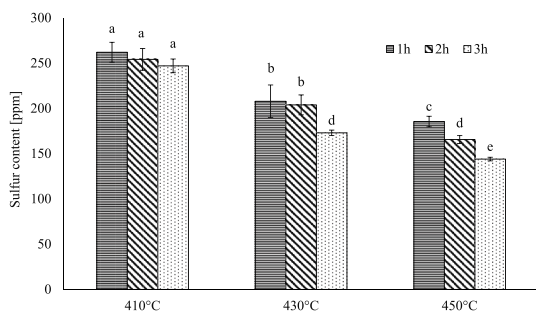


Fig. 1. Effect of temperature and time on the sulphur content of crude pyrolysis oil obtained using 15 mL microreactors. The average values of three replicates are shown with error bars representing the standard deviation. Means annotated with the same letter are statistically similar at a 95% confidence level.

37% HCl was added until the pH reached 2–3. pH values were determined using colorpHast indicator strips (Fisher Scientific; Fair Lawn, NJ, USA). The upper phase, which contained the unreacted fatty acids, was then recovered, and characterized through chromatographic analysis.

2.2.4. Analytical methods

The fatty acids feedstock (before and after any treatments) and crude pyrolysis product were subjected to gas chromatography (GC) analyses to determine their compositions. Each sample was prepared by dissolving 200 μg of liquid into 1 mL of pentane and adding 50 mg of methyl decanoate as an internal standard. After this, 200 μL of the solution were diluted with diazomethane (around 1 mL) until gas evolution could no longer be detected. The samples were then analyzed using a gas chromatograph coupled to a flame ionization detector and mass spectrometer (Agilent 6890N GC, 5975B mass spectrometer; (Agilent Technologies, Santa Clara, California, USA)). The details of the instruments, supplies and conditions used are reported elsewhere [45]. Peak identification was performed through comparison with the NIST 2011 mass spectral library and the recognition of fragmentation patterns of the mass spectra. After identification through mass spectroscopy, the amounts of free fatty acids, aromatics, saturated and unsaturated hydrocarbons were calculated based on the flame ionization peak areas using nonadecanoic acid as internal standard and reported as weight percentage.

Sulphur content determination was performed in the Natural Resources Analytical Laboratory (Department of Chemistry, University of Alberta). 2–5 mg of samples were processed using a microwave-assisted nitric acid digestion performed with a MARS 5 microwave system (CEM, Matthews, NC) and 5 mL of trace-metal grade HNO_3 . Samples were then diluted to a final total volume of 25 mL and analyzed using a ThermoCAP6000 series inductively coupled plasma-optical emission spectrometer (Thermo Fisher Scientific, Cambridge, United Kingdom) with Yttrium as an internal standard to correct for any potential matrix effects in the samples. Final analyte values were reported after this correction factor had been applied.

2.2.5. Statistical analysis

Statistical analyses were conducted, and ANOVA with a significance level of 0.05 ($p < 0.05$) were performed by using Excel™ (Microsoft Corp).

3. Results and discussion

3.1. Effect of pyrolysis on sulphur content

After pyrolysis of the fatty acid-enriched organic fraction produced through hydrolysis of brown grease, Omidghane et al. [13] determined that the liquid product generated contained 239 ± 21 ppm sulphur, which is well above the 10 ppm allowable in transportation fuels in the

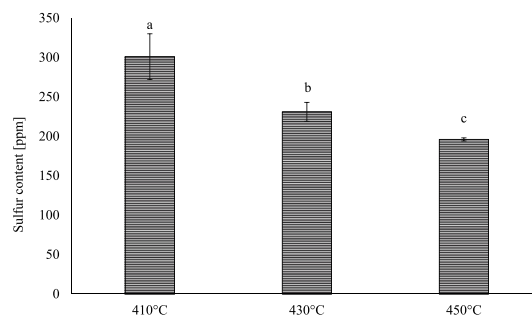


Fig. 2. Sulphur content in crude pyrolysis oil recovered after pyrolysis for 1 h at 1 L scale. The feedstock for pyrolysis reactions was the fatty acid-enriched organic phase recovered after hydrolysis of brown grease using biosolids. The average of triplicate experiments is shown, with the error bars representing the calculated standard deviation. Means annotated with the same letter are statistically similar at a 95% confidence level.

United States and the European Union [16]. To determine whether sulphur content in the crude pyrolysis oil is affected by changes in pyrolysis conditions, the fatty acids feedstock was subjected to pyrolysis in microreactors at different temperatures and times. As shown in Fig. 1, the crude liquid pyrolysis product collected at 410 °C did not show any correlation between processing time and sulphur content, with all three treatment times having statistically similar sulphur concentrations ($p < 0.05$). Conversely, at a temperature of 430 ± 18 ppm after a 1 h treatment to 173 ± 3 ppm after 3 h. The influence of temperature was more pronounced at 450 °C; the sulphur content decreased significantly with increasing treatment time. According to a two-way ANOVA test, these results suggest that both time and temperature affected the sulphur concentration, but in the range of 410 °C–450 °C, increasing temperature reduced sulphur concentration to a greater degree than increasing the reaction time from 1 h to 3 h.

The process was then scaled up using a 1 L batch reactor. In these experiments, the pyrolysis reactions were allowed to proceed for 1 h at 410, 430, or 450 °C. As observed in Fig. 2, and similar to what was observed at the 15 mL microreactor scale (Fig. 1), the sulphur content of the liquid pyrolysis product decreased with increasing temperature. Specifically, the sulphur content dropped from 301 ± 29 ppm at 410 °C, to 231 ± 12 ppm at 430 °C, and finally to 196 ± 2 ppm at 450 °C. It should be noted that at the 1 L scale, it took much longer to reach the desired temperatures compared with the microreactors where thermal steady state could be reached almost instantaneously. In fact, the 1 L batch reactor required 1.5 h to reach the desired temperature, meaning that its contents were heated for a substantial time, which could impact reaction kinetics. Nevertheless, these data further support the notion that increasing temperatures can reduce sulphur content in the crude liquid pyrolysis product.

Given the low oxidation state of sulphur containing compounds typically found in biosolids [46,47] and their associated bond energies [48,49], it is reasonable to presume that homolytic cleavage of the S–S bond (74 kcal/mol) and heterolytic cleavage of the C–S bond (69–75 kcal/mol) represents the first step of radical degradation. Conversely, heterolytic cleavage of the S–H bond (92 kcal/mol) requires relatively higher temperatures at which the C–C bond (83–85 kcal/mol) is also undergoing massive radical degradation. It should also be noted that although the presence of thiol radicals could promote rearrangement into thiols and sulfides, the frequency of these reactions during pyrolysis is negligible compared to the degradation of C–S/S–S bonds. However, the relatively mild reaction temperatures used in this study implies the formation of thiols and sulfides could occur, leading to retention of additional sulphur in the crude pyrolysis product.

Furthermore, as reported by Guo et al. [50], the formation of volatile sulphur-containing compounds is affected by the presence of CO_2 that

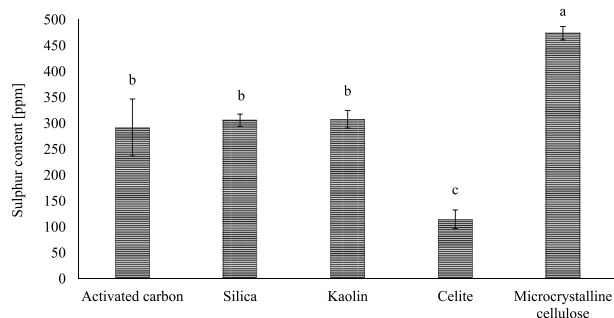


Fig. 3. Desulphurization of fatty acids recovered after hydrolysis of brown grease using biosolids as water replacement. In these experiments, a micellar system was employed using activated carbon, silica, kaolin, celite, or microcrystalline cellulose (MCC) as adsorbents. The averages of triplicate experiments are shown, with error bars representing the standard deviation. Means annotated with the same letter are statistically similar at a 95% confidence level.

promotes C–S bond cleavage. The pyrolysis of fatty acids is well known to generate substantial amounts of CO and CO₂ from carboxylic functionalities degradation that generally display a direct relationship with temperature [7,12,44,45]. On the hand, the formation of H₂S from the pyrolysis of sulphur containing compounds such as waste tires has also been shown [51,52]. Thus, a plausible mechanism for the sulphur content reduction in the liquid pyrolysis product could be that the increase in CO₂ that occurs with increasing pyrolysis temperature promotes H₂S formation. Any H₂S formed during pyrolysis can be removed from crude pyrolysis product and collected with gaseous fractions using adsorption or hydrodesulphurization [53–55]. Although the pyrolysis process resulted in a significant decrease in the sulphur content of the liquid product under the conditions employed in this study, the sulphur content was still well above the maximum allowed for automotive fuels. Thus, additional sulphur removal steps would be necessary to reduce sulphur content to acceptable levels.

3.2. Solid liquid extraction of sulphur compounds from pyrolytic oils

Initial experiments focused on the use of adsorbents to lower sulphur content in the fatty acids feedstock before pyrolytic conversion. The fatty acids feedstock was treated with an alkaline solution and directly mixed with various adsorbents. The use of alkaline conditions promoted deprotonation of the carboxyl groups present in fatty acids, along with any thiol groups, allowing for improved interaction of these deprotonated species with the adsorbents. However, deprotonated long chain fatty acids tend to form micellar structures that do not interact as easily with the adsorbents, which may facilitate targeted removal of deprotonated thiol groups that are associated with the aqueous phase. Several

adsorbents were examined for sulphur extraction purposes including high surface area porous materials (activated carbon, silica, kaolin, and Celite) as well as a biopolymer (microcrystalline cellulose) as reported in Fig. 3.

The use of activated carbon, silica and kaolin led to an appreciable reduction of sulphur content from 465 ± 6 ppm in the untreated fatty acids feedstock to 292 ± 55, 306 ± 12 and 308 ± 17 ppm, respectively. Celite showed the best activity leading to a reduction of sulphur content to 115 ± 18 ppm. Conversely, microcrystalline cellulose did not show any appreciable activity. It is possible that under the strong alkaline conditions used for these experiments, the microcrystalline cellulose was subjected to hydrolytic degradation [54] thus, rendering it ineffective. All of the adsorbents used retained material from the fatty acids feedstock as evidenced by the change in colour and increase of weight (~10–15% of the total mass of the adsorbents). It should also be noted that when activated carbon was used, carbon particles remained in the liquid fraction recovered after centrifugation, even when higher speeds (11,180×g) were used. It is not yet known if the presence of carbon particles would impact the quality of the liquid product generated through subsequent pyrolysis.

A second adsorption approach was also employed in which the fatty acids feedstock was placed in a flask connected to a Soxhlet extractor that contained various adsorbents in the chamber. In this way, low boiling sulphur compounds (*i.e.* dimethylsulfide, dimethyldisulfide, diethylsulfide, methylthiol) were boiled away from the fatty acids feedstock and captured after condensation by the adsorbent, while some high boiling compounds were carried off by the steam stream but the majority were retained in the bottom of the flask. Again, several different adsorbents were tested including activated carbon, Celite, microcrystalline cellulose, along with some ion exchange resins with different functionalities (anionic and cation resins) as shown in Fig. 4.

For activated carbon, the Soxhlet method resulted in a similar level of sulphur reduction as compared with the direct mixing procedure (365 ± 42 ppm vs. 292 ± 55 ppm, respectively). Conversely, the Soxhlet extraction method resulted in poorer sulphur removal when Celite was employed as an adsorbent. On the other hand, a slightly improved extraction was observed when microcrystalline cellulose was used. This confirms that the effectiveness of sulphur removal depends on both the method and adsorbent employed. The use of anionic resins (*i.e.* Amberlite IRA67 and IRA400) resulted in a decrease in sulphur content to around 350 ppm, with the exception of Amberlyst A21, which promoted even better desulphurization (247 ± 29 ppm). A similar result (224 ± 17 ppm) was achieved using the cationic resin Amberlite IRC 86. This is evidence that sulphur species are weakly dissociated, and the driving force of the adsorption was not due to ionic interactions but rather because of weak surface forces.

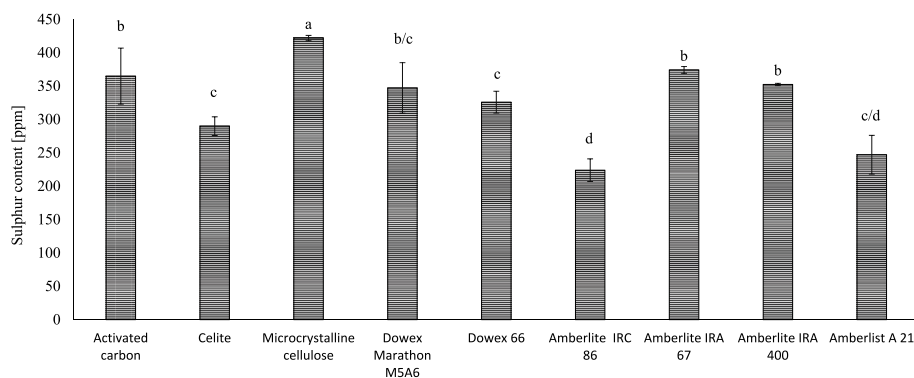


Fig. 4. Desulphurization using a Soxhlet apparatus with a cartridge filled with activated carbon, celite, microcrystalline cellulose, Dowex Marathon M5A6, Dowex 66, Amberlite IRC86, Amberlite IRA67, Amberlite IRA400, or Amberlyst A21. The averages of triplicate experiments are shown, with error bars representing the standard deviation. Means annotated with the same letter are statistically similar at a 95% confidence level.

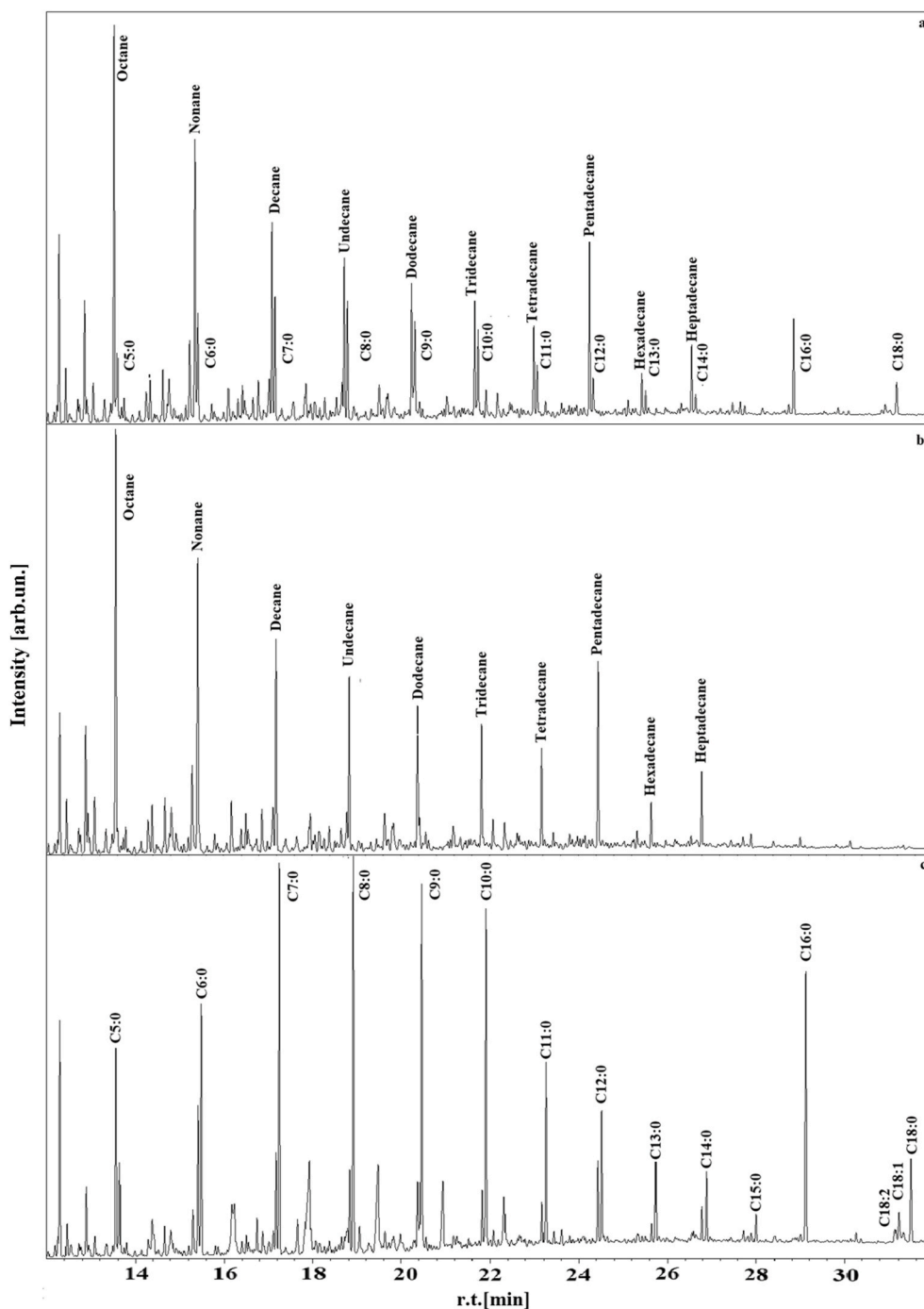


Fig. 5. GC chromatograms (in the range of 12–32 min, avoiding the signal of the solvent) generated from various fractions during the liquid-liquid extraction process. Crude pyrolysis oil (a) obtained through pyrolysis at 410 °C was subjected to a two-step liquid-liquid extraction process, to generate a purified organic fraction (b). The aqueous stream obtained in this process was acidified to facilitate recovery of the unreacted fatty acids (c).

3.4. Liquid-liquid extractions of sulphur compounds from pyrolytic oils

Desulphurization of crude liquid pyrolysis product derived from a fatty acids feedstock was also investigated using a liquid-liquid extraction procedure. This two-step process is based on the treatment of crude pyrolysis product with an alkaline solution (pH 12–13) followed by a water extraction that allows simultaneous removal of residual fatty acids and thiols, thus producing a purified organic fraction. The alkaline aqueous phase recovered in the second extraction step was also isolated and acidified to pH 2–3 with acid (HCl) in order to recover the fatty acids that could be used as feedstock for pyrolysis or fractionated and purified

for high value applications. Each of the recovered fractions was analyzed using gas chromatography (Fig. 5); the sulphur content in these fractions was also quantified (Table 2).

The liquid-liquid extraction resulted in excellent desulphurization of the crude liquid pyrolysis product, regardless of the temperature at which the pyrolysis was performed. The extractable sulphur compounds were most likely thiol-containing compounds that were present in the fatty acids feedstock or generated during pyrolysis from reductive degradation of disulfide compounds. This effect was most pronounced at 410 °C where the liquid-liquid extraction resulted in a decrease in sulphur concentration from 301 ± 29 to 18 ± 3 ppm. As the temperature

Table 2

Composition and mass balance of the fractions recovered after liquid-liquid extraction of the crude pyrolysis oil produced using a 1 L reactor for 1 h at different temperatures. The error values represent the standard deviation calculated according to the values of three replicate experiments of chromatographic analysis.

Entry	Fraction	Sulphur [ppm]	Recovery [wt%]	Composition		
				Aromatics [wt%]	Fatty acids [wt%]	Hydrocarbons [wt%]
410	Crude pyrolysis oil	301 ±29	–	7.8 ±0.3	28.4 ±0.9	55.7 ±2.2
	Organic fraction	18 ±3	80.1 ±0.4	9.6 ±0.4	Not detected ^a	82.7 ±2.0
	Recovered fatty acids	146 ±21	13.0 ±0.3	1.2 ±0.4	75.6 ±0.8	17.1 ±0.6
430	Crude pyrolysis oil	231 ±12	–	11.7 ±0.7	22.7 ±0.9	59.9 ±1.8
	Organic fraction	30 ±3	84.1 ±0.3	13.3 ±0.9	Not detected ^a	78.7 ±2.6
	recovered fatty acids	215 ±12	6.3 ±0.2	3.4 ±0.8	69.3 ±1.3	19.8 ±0.5
450	Crude pyrolysis oil	196 ±12	–	14.7 ±0.3	11.2 ±0.6	72.9 ±1.2
	Organic fraction	48 ±4	87.2 ±0.5	26.7 ±1.1	Not detected ^a	66.4 ±2.6
	recovered fatty acids	139 ±15	4.9 ±0.1	4.2 ±0.2	74.4 ±2.9 ^b	14.5 ±0.6

^a Each extraction was repeated three times and unreacted fatty acids were observed in trace amounts in some organic phase (up to 0.2–0.3 wt%).

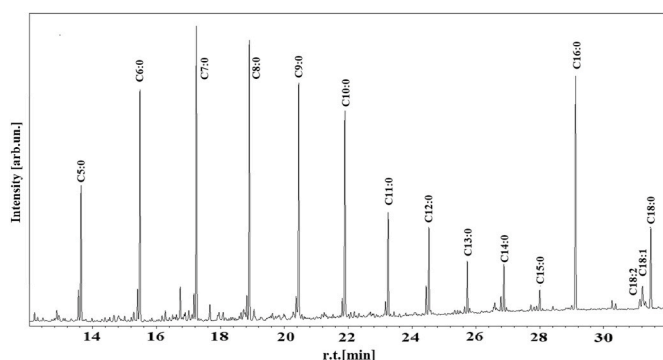


Fig. 6. Chromatogram (12–32 min, avoiding the signal of the solvent) of the hexane extracted material from the aqueous phase obtained after both liquid-liquid extraction of crude pyrolysis oil (410 °C, 1 h) and acidification for fatty acids removal.

of pyrolysis increased, the effectiveness of the liquid-liquid extraction dropped, with sulphur levels rising to 30 ± 3 ppm at 430 °C and 48 ± 4 ppm at 450 °C. Interestingly, the sulphur concentration increased in the organic fraction with increasing pyrolysis temperature even though the sulphur content in the original crude liquid pyrolysis product decreased as the pyrolysis temperature was elevated. Since increasing the pyrolysis temperature is known to result in the formation of more aromatic compounds (Table 2), it is reasonable to suggest that at higher pyrolysis temperatures, more benzothiophenes and other sulphur-containing aromatics are produced. This would lead to more sequestration of sulphur in the organic fraction obtained after liquid-liquid extraction.

The recovered fatty acids fractions obtained through acidification of the aqueous phase after liquid-liquid extraction contained relatively large amounts of hydrocarbons (from $14.5 \pm 0.6\%$ to $19.8 \pm 0.5\%$). As mentioned above in section 3.2, the alkaline treatment promotes fatty acids to form micelles, which may have engulfed non-polar carbons such as hydrocarbons leading to the partitioning of hydrocarbons into the aqueous phase. At first glance, this may seem detrimental, however, since the recovered fatty acids fraction can also be incorporated as a pyrolysis feedstock together with the fatty acids feedstock, the hydrocarbon content would not be lost and could still be recovered for fuel applications. To confirm this theory, the fatty acids recovered from crude pyrolysis product (410 °C) were tested as pyrolysis feedstock using microreactors and a 1 h processing time. The sulphur content of the

liquid product recovered from this pyrolysis reaction was 75 ppm and the composition showed a massive presence of unreacted fatty acids (47.1 ± 1.3 wt%), as well as appreciable amounts of hydrocarbons (39.6 ± 0.9 wt%) and aromatics (6.7 ± 0.6 wt%).

As shown in Fig. 6, the aqueous phase contained some fatty acids and trace amounts of aromatic compounds, indicating incomplete recovery of fatty acids. This material likely accounts for the mass loss evident in the “Recovery” column of Table 2.

Next, the crude pyrolysis product obtained at 410 °C using a 1 L reactor was distilled and three fractions were collected: 1) Distillate recovered in the temperature range of room temperature (RT) to 100 °C (16.5 ± 0.3 wt%); 2) Distillate recovered in the temperature range of 100 °C–200 °C (35.4 ± 0.4 wt%); 3) Undistilled residue (44.4 ± 0.6 wt%). Liquid-liquid extraction was then performed on the three fractions recovered after distillation of crude pyrolysis oil. The levels of sulphur, hydrocarbons, and aromatics present before and after liquid-liquid extraction of the distillates and residue are shown in Fig. 7.

For all three fractions recovered after distillation of crude pyrolysis oil, liquid-liquid extraction dramatically reduced the amount of sulphur from 307 ± 10 ppm to 15 ± 4 ppm (RT to 100 °C), 333 ± 13 ppm to 23 ± 6 ppm (100 °C–200 °C), and 267 ± 18 ppm to 39 ± 8 (undistilled residue). For the fractions recovered from RT to 100 °C and 100 °C–200 °C, there were very small but significant differences in the amounts of hydrocarbons found in the organic fractions before and after liquid-liquid extraction. Conversely, there was a large increase in the weight percentage of hydrocarbons observed for the undistilled residue following liquid-liquid extraction. This was attributed to the high fatty acid content of the undistilled residue (49.8 ± 1.3 wt%) that was subsequently removed through liquid-liquid extraction. Consistent with this, the recovery of the organic fraction following liquid-liquid extraction of the undistilled residue was only 44.3 ± 1.1 wt%, with the fatty acid fraction comprising 51.7 ± 1.3 wt%. In comparison, the percent recovery of the organic fraction recovered after liquid to liquid extraction of the RT to 100 °C and 100 °C–200 °C fractions were 95.4 ± 0.6 and 90.5 ± 0.9 , respectively. The fatty acid fraction (88.9 ± 1.4 wt% fatty acids) recovered after liquid-liquid extraction of the undistilled residue contained 201 ± 11 ppm sulphur, 9.6 ± 1.3 wt% hydrocarbons and $1.4 \pm 0.8\%$ aromatics. Regarding aromatics, liquid-liquid extraction reduced the levels of aromatics in the organic fraction extracted from the RT to 100 °C fraction and the undistilled residue, but did not change the weight percentage of aromatics in the organic fraction recovered from 100 °C to 200 °C.

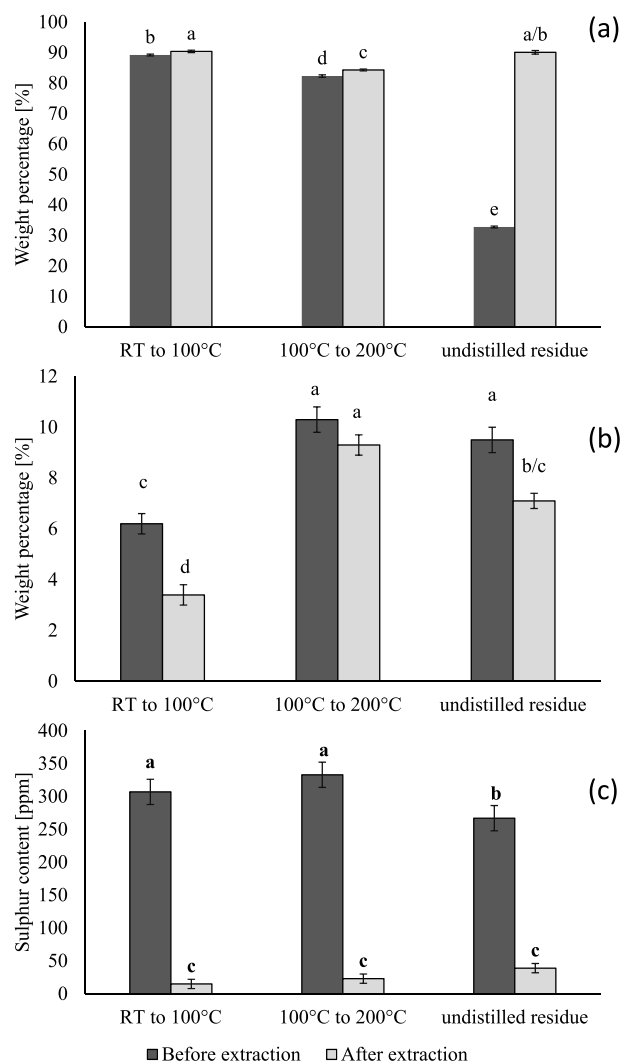


Fig. 7. Amount of hydrocarbons (A), aromatics (B), and sulphur (C) in the three fractions recovered after distillation of crude pyrolysis oil (1 L reactor, 410 °C, 1 h). The levels were measured in the organic fraction before and after liquid-liquid extraction. The error values represent the standard deviation calculated according to the values of three replicated experiments of chromatographic analysis. Means annotated with the same letter are statistically similar at a 95% confidence level.

4. A comparison between desulphurization techniques of pyrolytic oils

Desulphurization procedures have been diffusely studied for the upgrading of pyrolytic oils produced from waste tires. For this purpose, two main routes have been investigated: i) hydrodesulphurization; and ii) oxidative desulphurization.

Hydrodesulphurization is a well-established process in the oil industry, and it is based on the reduction of sulphur containing compounds to H_2S by using hydrogen over a catalytic system. This technique was used by Jantaraksa et al. [57] to remove up to 87% of sulphur from tires-derived pyrolytic oil using a Ni/Mo catalyst supported onto alumina operating at 400 °C. Similarly, Jiang et al. [58] used an Fe doped Ni supported onto an organic resin catalyst achieving a desulphurization of up to 91% at 300 °C. Saleh et al. [59] developed a Mo/Co catalyst supported onto carbon achieving a desulphurization of up to 98% in a packed bed reactor at 340 °C. In another study, Hita et al. [60] reported a 91% desulphurization when a Mo/Co catalyst supported on zeolite was used.

Oxidative desulphurization is based on the conversion of sulphur

Table 3

Comparative analysis of main procedures for desulphurization of pyrolytic oils.

Desulphurization technique	System	Desulphurization Achieved	Ref
Hydrodesulphurization	Ni/Mo catalyst supported on to γ Al_2O_3	87%	[55]
	Fe doped Ni SBA-15	91%	[56]
	Mo/Co supported onto carbon	98%	[57]
	Mo/Co supported onto zeolite	91%	[58]
Oxidative desulphurization	Fe nanoparticles anchored onto carbon	60%	[59]
	Formic acid and Al_2O_3	84%	[60]
Distillation/liquid-liquid extraction	$H_3PW_{12}O_{40} \cdot 20H_2O$	99%	[61]
	Biphasic extraction	94%	Present work

containing compounds into sulphone species that are extractable in polar solvents. The oxidation process is generally performed by using oxygenated water and Fenton and Fenton-like catalysts. Tamborrino et al. [61] used anchored iron nanoparticles on carbon as catalyst for desulphurization of high sulphur content tire oil. The authors reported a desulphurization of 60% hypothesising a poor efficiency of sulphones extraction in water media. Nonetheless, Zhang et al. [62] achieved a desulphurization of up to 84% by using a catalytic system based on alumina and formic acid. Alternatively, Chen et al. [63] developed an ultrasound based approach using $H_3PW_{12}O_{40} \cdot 20H_2O$ as catalyst and achieved a remarkably desulphurization of up to 99%, but only after an extraction of sulphones using alumina.

As summarized in Table 3, the combination of distillation and liquid-liquid extraction reported in the present work is highly competitive with the best methods reported in literature. A potential drawback is the limited applicability to acid rich oil that allow the formation of homogenous/biphasic systems. Nevertheless, this approach has been proven to be as a solid technique for sulphur removal from pyrolytic fractions recovered after pyrolysis of fatty acids feedstock, without requiring the high temperature of desulphurization or the large amounts of reagents in oxidative desulphurization.

5. Conclusions

While incorporation of biosolids into lipid pyrolysis presents issues surrounding the sulphur content of the fatty acids feedstock and crude pyrolysis oils, increasing the reaction temperature led to a lower sulphur content in the crude pyrolysis oil. Similarly, increasing processing time also lowered the sulphur concentration of the crude pyrolysis oil, with its effect becoming more appreciable at higher temperatures (430 °C and 450 °C). As another approach for desulphurization, various pre-treatments were used to decrease the concentration of sulphur containing compounds in the fatty acids feedstock. Extraction of sulphur compounds was shown using different adsorbers through direct mixing with the fatty acids feedstock, or using a Soxhlet approach, with the best performance achieved using Celite and the direct mixing protocol. Despite the positive results achieved using direct mixing, recovery of the adsorbers was more challenging and better facilitated through use of the Soxhlet protocol. Using a liquid-liquid extraction process for oxidative desulphurization enabled simple recovery of unreacted fatty acids that could be converted to hydrocarbon fuels through a subsequent pyrolysis. The liquid-liquid extraction approach was the most effective of the methods here discussed leading to a fuel with a very low sulphur content of up to 18 ± 3 ppm and down to 15 ± 4 ppm if it was performed after distillation. Taken together, the data presented demonstrate several promising options for reducing sulphur content in the final liquid

product derived from lipid pyrolysis using biosolids and brown grease as feedstock.

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.

Funding

This work was supported through generous contributions from the Natural Sciences and Engineering Research Council of Canada (NSERC) [grant number RGPIN 298352-2013], Mitacs Canada [grant number MI MA IT05367], BioFuelNet Canada [grant number NCEBFNC 6F], Agriculture and Agri-Food Canada's Canadian Agricultural Partnership [Bressler AgriScience Cluster project], and our collaborators from Forge Hydrocarbons Inc. who also hosted Mattia Bartoli as an intern.

CRediT authorship contribution statement

Mattia Bartoli: Methodology, Formal analysis, Investigation, Writing – original draft. **Justice Asomaning:** Methodology, Writing – review & editing. **Lin Xia:** Methodology, Investigation. **Michael Chae:** Supervision, Writing – review & editing. **David C. Bressler:** Supervision, Conceptualization, Funding acquisition, Project administration.

Acknowledgments

We would like to extend our gratitude to the Natural Resources Analytical Laboratory (Chemistry Department, University of Alberta), the City of Edmonton, EPCOR Water Services Inc., and Suez for their support throughout the project.

References

- [1] S. Shafiee, E. Topal, When will fossil fuel reserves be diminished? *Energy Pol.* 37 (1) (2009) 181–189.
- [2] M. Asif, T. Muneer, Energy supply, its demand and security issues for developed and emerging economies, *Renew. Sustain. Energy Rev.* 11 (7) (2007) 1388–1413.
- [3] J.P. Dorian, H.T. Franssen, D.R. Simbeck, Global challenges in energy, *Energy Pol.* 34 (15) (2006) 1984–1991.
- [4] R. Kajaste, Chemicals from biomass—managing greenhouse gas emissions in biorefinery production chains—a review, *J. Clean. Prod.* 75 (2014) 1–10.
- [5] F. Cherubini, The biorefinery concept: using biomass instead of oil for producing energy and chemicals, *Energy Convers. Manag.* 51 (7) (2010) 1412–1421.
- [6] D. Chiamonti, M. Prussi, M. Buffi, A.M. Rizzo, L. Pari, Review and experimental study on pyrolysis and hydrothermal liquefaction of microalgae for biofuel production, *Appl. Energy* 185 (2017) 963–972.
- [7] I. Espinosa-Gonzalez, J. Asomaning, P. Mussone, D.C. Bressler, Two-step thermal conversion of oleaginous microalgae into renewable hydrocarbons, *Bioresour. Technol.* 158 (2014) 91–97.
- [8] A. Atabani, A. Silitonga, H. Ong, T. Mahlia, H. Masjuki, I.A. Badruddin, H. Fayaz, Non-edible vegetable oils: a critical evaluation of oil extraction, fatty acid compositions, biodiesel production, characteristics, engine performance and emissions production, *Renew. Sustain. Energy Rev.* 18 (2013) 211–245.
- [9] L. Meher, D.V. Sagar, S. Naik, Technical aspects of biodiesel production by transesterification—a review, *Renew. Sustain. Energy Rev.* 10 (3) (2006) 248–268.
- [10] C.M. Prado, N.R. Antoniosi Filho, Production and characterization of the biofuels obtained by thermal cracking and thermal catalytic cracking of vegetable oils, *J. Anal. Appl. Pyrol.* 86 (2) (2009) 338–347.
- [11] K. Maher, D. Bressler, Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals, *Bioresour. Technol.* 98 (12) (2007) 2351–2368.
- [12] J. Asomaning, P. Mussone, D.C. Bressler, Two-stage thermal conversion of inedible lipid feedstocks to renewable chemicals and fuels, *Bioresour. Technol.* 158 (2014) 55–62.
- [13] M. Omidghane, M. Bartoli, J. Asomaning, L. Xia, M. Chae, D.C. Bressler, Pyrolysis of fatty acids derived from hydrolysis of brown grease with biosolids, *Environ. Sci. Pollut. Res.* (2020) 1–11.
- [14] M.J. McFarland, *Biosolids Engineering*, McGraw-Hill Professional Publishing 2000.
- [15] SOR/2002-254, sulphur in diesel fuel regulations. <http://laws-lois.justice.gc.ca/eng/regulations/SOR-2002-254/index.html>, 2017.
- [16] D. Iruretagoyena, R. Montesano, Selective Sulfur Removal from Liquid Fuels Using Nanostructured Adsorbents, *Nanotechnology in Oil and Gas Industries*, Springer, 2018, pp. 133–150.
- [17] I. Babich, J. Moulijn, Science and technology of novel processes for deep desulfurization of oil refinery streams: a review, *Fuel* 82 (6) (2003) 607–631.
- [18] V.C. Srivastava, An evaluation of desulfurization technologies for sulfur removal from liquid fuels, *RSC Adv.* 2 (3) (2012) 759–783.
- [19] S. Brunet, D. Mey, G. Pérot, C. Bouchy, F. Diehl, On the hydrodesulfurization of FCC gasoline: a review, *Appl. Catal. Gen.* 278 (2) (2005) 143–172.
- [20] H. Shang, W. Du, Z. Liu, H. Zhang, Development of microwave induced hydrodesulfurization of petroleum streams: a review, *J. Ind. Eng. Chem.* 19 (4) (2013) 1061–1068.
- [21] P. Vasudevan, J.G. Fierro, A review of deep hydrodesulfurization catalysis, *Catal. Rev.* 38 (2) (1996) 161–188.
- [22] M. Vrinat, The kinetics of the hydrodesulfurization process—a review, *Appl. Catal.* 6 (2) (1983) 137–158.
- [23] M.L. Vrinat, The kinetics of the hydrodesulfurization process - a review, *Appl. Catal.* 6 (2) (1983) 137–158.
- [24] X. Ma, K. Sakanishi, I. Mochida, Hydrodesulfurization reactivities of various sulfur compounds in diesel fuel, *Ind. Eng. Chem. Res.* 33 (2) (1994) 218–222.
- [25] I. Mochida, K.-H. Choi, An overview of hydrodesulfurization and hydrogenation, *J. Jpn. Petrol. Inst.* 47 (3) (2004) 145–163.
- [26] J. Campos-Martin, M. Capel-Sanchez, P. Perez-Presas, J. Fierro, Oxidative processes of desulfurization of liquid fuels, *J. Chem. Technol. Biotechnol.* 85 (7) (2010) 879–890.
- [27] C. Dai, J. Zhang, C. Huang, Z. Lei, Ionic liquids in selective oxidation: catalysts and solvents, *Chem. Rev.* 117 (10) (2017), 6929–6883. doi.org/10.1021/acs.chemrev.7b00030.
- [28] R. Zaykina, Y.A. Zaykin, G. Mirkin, N. Nadirov, Prospects for irradiation processing in the petroleum industry, *Radiat. Phys. Chem.* 63 (3) (2002) 617–620.
- [29] A. Ibrahim, S.B. Xian, Z. Wei, Desulfurization of FCC gasoline by solvent extraction and photooxidation, *Petrol. Sci. Technol.* 21 (9–10) (2003) 1555–1573.
- [30] H. Mei, B. Mei, T.F. Yen, A new method for obtaining ultra-low sulfur diesel fuel via ultrasound assisted oxidative desulfurization, *Fuel* 82 (4) (2003) 405–414.
- [31] W. Wang, S. Wang, Y. Wang, H. Liu, Z. Wang, A new approach to deep desulfurization of gasoline by electrochemically catalytic oxidation and extraction, *Fuel Process. Technol.* 88 (10) (2007) 1002–1008.
- [32] S. Liu, B. Wang, B. Cui, L. Sun, Deep desulfurization of diesel oil oxidized by Fe (VI) systems, *Fuel* 87 (3) (2008) 422–428.
- [33] Y. Shiraishi, K. Tachibana, T. Hirai, I. Komasa, Desulfurization and denitrogenation process for light oils based on chemical oxidation followed by liquid–liquid extraction, *Ind. Eng. Chem. Res.* 41 (17) (2002) 4362–4375.
- [34] S. Kumar, V.C. Srivastava, R. Badoni, Oxidative desulfurization by chromium promoted sulfated zirconia, *Fuel Process. Technol.* 93 (1) (2012) 18–25.
- [35] J.L. García-Gutiérrez, G.A. Fuentes, M.E. Hernández-Terán, F. Murrieta, J. Navarrete, F. Jiménez-Cruz, Ultra-deep oxidative desulfurization of diesel fuel with H₂O₂ catalyzed under mild conditions by polymolybdates supported on Al₂O₃, *Appl. Catal. Gen.* 305 (1) (2006) 15–20.
- [36] S. Velu, X. Ma, C. Song, Selective adsorption for removing sulfur from jet fuel over zeolite-based adsorbents, *Ind. Eng. Chem. Res.* 42 (21) (2003) 5293–5304.
- [37] R.T. Yang, A.J. Hernández-Maldonado, F.H. Yang, Desulfurization of transportation fuels with zeolites under ambient conditions, *Science* 301 (5629) (2003) 79–81.
- [38] L. Deng, B. Lu, J. Li, G. Lv, S. Du, J. Shi, Y. Yang, Effect of pore structure and oxygen-containing groups on adsorption of dibenzothiophene over activated carbon, *Fuel* 200 (2017) 54–61.
- [39] Y.A. Alhamed, H.S. Bamufleh, Sulfur removal from model diesel fuel using granular activated carbon from dates' stones activated by ZnCl₂, *Fuel* 88 (1) (2009) 87–94.
- [40] W. Li, H. Tang, T. Zhang, Q. Li, J. Xing, H. Liu, Ultra-deep desulfurization adsorbents for hydrotreated diesel with magnetic mesoporous aluminosilicates, *AIChE J.* 56 (5) (2010) 1391–1396.
- [41] W. Li, Q. Liu, J. Xing, H. Gao, X. Xiong, Y. Li, X. Li, H. Liu, High-efficiency desulfurization by adsorption with mesoporous aluminosilicates, *AIChE J.* 53 (12) (2007) 3263–3268.
- [42] J. Fan, G. Wang, Y. Sun, C. Xu, H. Zhou, G. Zhou, J. Gao, Research on reactive adsorption desulfurization over Ni/ZnO–SiO₂–Al₂O₃ adsorbent in a fixed-fluidized bed reactor, *Ind. Eng. Chem. Res.* 49 (18) (2010) 8450–8460.
- [43] L. Xia, M. Chae, J. Asomaning, M. Omidghane, C. Zhu, D.C. Bressler, Incorporation of biosolids as water replacement in a two-step renewable hydrocarbon process: hydrolysis of Brown grease with biosolids, *Waste Biomass Valoriz.* (2019) 1–12.
- [44] J. Asomaning, P. Mussone, D.C. Bressler, Thermal deoxygenation and pyrolysis of oleic acid, *J. Anal. Appl. Pyrol.* 105 (2014) 1–7.
- [45] M. Omidghane, E. Jenab, M. Chae, D.C. Bressler, Production of renewable hydrocarbons by thermal cracking of oleic acid in the presence of water, *Energy Fuels* 31 (9) (2017) 9446–9454.
- [46] M.J. Higgins, Y.-C. Chen, D.P. Yarosz, S.N. Murthy, N.A. Maas, D. Glindemann, J. T. Novak, Cycling of volatile organic sulfur compounds in anaerobically digested biosolids and its implications for odors, *Water Environ. Res.* 78 (3) (2006) 243–252.
- [47] X.-q. Li, D.G. Brown, W.-x. Zhang, Stabilization of biosolids with nanoscale zero-valent iron (nZVI), *J. Nanoparticle Res.* 9 (2) (2007) 233–243.
- [48] S.W. Benson, Thermochemistry and kinetics of sulfur-containing molecules and radicals, *Chem. Rev.* 78 (1) (1978) 23–43.
- [49] M. Szwarc, The determination of bond dissociation energies by pyrolytic methods, *Chem. Rev.* 47 (1) (1950) 75–173.
- [50] H. Guo, X. Wang, F. Liu, M. Wang, H. Zhang, R. Hu, Y. Hu, Sulfur release and its transformation behavior of sulfur-containing model compounds during pyrolysis under CO₂ atmosphere, *Fuel* 206 (2017) 716–723.

- [51] D. Susa, J. Haydary, Sulphur distribution in the products of waste tire pyrolysis, *Chem. Pap.* 67 (12) (2013) 1512–1526.
- [52] H. Hu, Y. Fang, H. Liu, R. Yu, G. Lou, W. Liu, A. Li, H. Yao, The fate of Sulphur during rapid pyrolysis of scrap tires, *Chemosphere* 97 (2014) 102–107.
- [53] S. Nishimura, M. Yoda, Removal of hydrogen sulfide from an anaerobic biogas using a bio-scrubber, *Water Sci. Technol.* 36 (6–7) (1997) 349–356.
- [54] J. Krischan, A. Makaruk, M. Harasek, Design and scale-up of an oxidative scrubbing process for the selective removal of hydrogen sulfide from biogas, *J. Hazard Mater.* 215 (2012) 49–56.
- [55] L. Chen, J. Huang, C.L. Yang, Absorption of H₂S in NaOCl caustic aqueous solution, *Environ. Prog. Sustain. Energy* 20 (3) (2001) 175–181.
- [56] L. Fan, M. Gharpuray, Y. Lee, *Biotechnology monographs, Cellul. Hydrol.* 3 (1987).
- [57] N. Jantaraksa, P. Prasassarakich, P. Reubroycharoen, N. Hinchiranan, Cleaner alternative liquid fuels derived from the hydrodesulfurization of waste tire pyrolysis oil, *Energy Convers. Manag.* 95 (2015) 424–434.
- [58] B. Jiang, T. Zhu, H. Song, F. Li, Hydrodeoxygenation and hydrodesulfurization over Fe promoted Ni₂P/SBA-15 catalyst, *J. Alloys Compd.* 806 (2019) 254–262.
- [59] T.A. Saleh, S.A. Al-Hammadi, I.M. Abdullahi, M. Mustaqeem, Synthesis of molybdenum cobalt nanocatalysts supported on carbon for hydrodesulfurization of liquid fuels, *J. Mol. Liq.* 272 (2018) 715–721.
- [60] I. Hita, A. Gutiérrez, M. Olazar, J. Bilbao, J.M. Arandes, P. Castaño, Upgrading model compounds and Scrap Tires Pyrolysis Oil (STPO) on hydrotreating NiMo catalysts with tailored supports, *Fuel* 145 (2015) 158–169.
- [61] V. Tamborrino, G. Costamagna, M. Bartoli, M. Rovere, P. Jagdale, L. Lavagna, M. Ginepro, A. Tagliaferro, Catalytic oxidative desulphurization of pyrolytic oils to fuels over different waste derived carbon-based catalysts, *Fuel* 296 (2021) 120693.
- [62] Q. Zhang, M. Zhu, I. Jones, Z. Zhang, D. Zhang, Desulfurization of spent tire pyrolysis oil and its distillate via combined catalytic oxidation using H₂O₂ with formic acid and selective adsorption over Al₂O₃, *Energy Fuels* 34 (5) (2020) 6209–6219.
- [63] T.-C. Chen, Y.-H. Shen, W.-J. Lee, C.-C. Lin, M.-W. Wan, The study of ultrasound-assisted oxidative desulfurization process applied to the utilization of pyrolysis oil from waste tires, *J. Clean. Prod.* 18 (18) (2010) 1850–1858.