Desulfurization of Low-Value Agricultural Lipid Feedstocks and the Resulting Diesel for Renewable Fuel Applications

by

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ABSTRACT

Generating energy is essential for global socio-economic development and fundamental for producing valuable goods and services. Fossil fuels are the predominant source of energy now. However, their limited supply and environmental harm from greenhouse gas emissions make them unsustainable, necessitating the need for eco-friendly, renewable fuels. Renewable energy, replenished naturally within a short time frame, offers a sustainable alternative. Among renewable sources, biomass, particularly non-edible lipid feedstocks like plant oils and animal fats, is especially promising due to its high energy density and simpler structure. Converting these lipids into biofuels is attractive for sustainable energy production, waste management, and public health benefits. These biofuels are compatible with existing infrastructure and possibly can address environmental and energy concerns.

Sulfur compounds are among the most common impurities in transportation fuels. Their emission during combustion poses serious environmental and health risks, including acid rain, ecosystem disruption, respiratory issues, and equipment corrosion. In response, global regulations mandate a sulfur content cap of around 15 ppm in diesel fuels, driving research into effective desulfurization techniques. Desulfurization is a process that efficiently removes sulfur from different types of samples. Therefore, this study focuses on removing sulfur compounds from poultry fat (100.0 ± 0.8 ppm), brown grease (515 ± 5 ppm), hardwood (1490 ± 40 ppm), and softwood (2040 ± 40 ppm) crude tall oils, to be used for renewable fuel applications.

The first approach assessed desulfurization techniques, including solvent extraction, oxidation, ultrasonication, and adsorption, to eliminate sulfur from feedstocks. Solvent extraction with water, acetonitrile, methanol, and diethylene glycol mono ethyl ether separated sulfur compounds based on polarity difference. The oxidative desulfurization method used glacial acetic acid and hydrogen peroxide to oxidize sulfur-containing compounds to sulfoxides and sulfones. The study investigated the influence of temperature, catalyst-oxidant molar ratio, and catalyst-oxidant concentration relative to feedstock on sulfur removal, achieving the highest removal at 90 °C, 1:3.57, and 36.5% w/w, respectively. Ultrasonic-assisted oxidative desulfurization using water significantly reduced sulfur levels in poultry fat through cavitation effects. The potential of adsorbents was explored in adsorptive desulfurization, with Al-MCM-41 exhibiting superior performance in poultry fat and brown grease despite separation challenges.

In summary, for poultry fat and brown grease, the most effective method was ultrasonic-assisted oxidative desulfurization and extractive desulfurization using water as a solvent, achieving sulfur removal efficiencies of 78.9 ± 0.4% (21.1 ± 0.3 ppm) and 50 ± 1% (257 ± 3 ppm), respectively. For hardwood and softwood crude tall oils, adsorptive desulfurization with raw bentonite clay was the most effective, with removal efficiencies of 49 ± 3% (760 ± 30 ppm) and 36 ± 2% (1300 ± 20 ppm), respectively.

The second approach of the study examined sulfur removal during the thermochemical conversion of non-edible lipid feedstocks into diesel equivalents. The process involved hydrolysis to break acylglycerols into free fatty acids, followed by pyrolysis, converting them into hydrocarbons. Caustic washing of pyrolyzed products reduced the sulfur content by separating the hydrocarbons from unconverted free fatty acids that could trap sulfur compounds. Distillation of caustic-washed samples refined diesel-equivalent products by enhancing purity and reducing sulfur content. Hence, the thermochemical conversion process significantly lowered sulfur content by 56 ± 1% in poultry fat-derived diesel (43.9 ± 0.6 ppm) and by 78.4 ± 0.4% in brown grease-derived diesel

(111 ± 2 ppm). The comprehensive method greatly improved the quality of the final diesel products, showcasing its ability to develop renewable fuel while protecting the environment.

The third approach extended the work from the first and second approaches by integrating the adsorptive desulfurization technique for diesel equivalents produced through thermochemical conversion. This method successfully decreased sulfur content in poultry fat-derived diesel using Amberlyst®-A21 and Al-MCM-41, reaching levels of 26 ± 1 ppm and 29 ± 2 ppm, with removal efficiencies of 41 ± 3% and 34 ± 6%, respectively.

In conclusion, this study of desulfurizing low-value agricultural lipid feedstocks and the resulting diesel for renewable fuel applications has yielded promising results that indicate the potential for practical applications. It emphasizes the importance of selecting the appropriate desulfurization technique based on the specific feedstock. Therefore, the findings of this research can potentially contribute to sustainable energy production and environmental protection from sulfur emissions.

PREFACE

This thesis is an original work by Frehiwot Tesfamariam Hailu. There is no part of this thesis has been previously published. All the experiments in this thesis were conducted in the Biorefining Conversion and Fermentation Laboratory at the University of Alberta and were discussed with Dr. David C. Bressler. Some sections of the paragraphs were edited using AI tools, including ChatGPT and Grammarly.

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List of Abbreviations

Al-MCM-41	Aluminum containing Mobile Composition of Matter Number 41
ASTM	American Society for Testing Materials
BT	Benzothiophene
CGSB	Canadian General Standards Board
CO	Carbon monoxide
CO_2	Carbon dioxide
COx	Oxides of Carbon
CTO	Crude Tall Oil
DAG	Diacylglycerol
DBT	Dibenzothiophene
EPA	Environmental Protection Agency
FFA	Free Fatty Acid
FID	Flame Ionization Detector
FTIR–ATR	Fourier transform infrared spectroscopy – attenuated total reflectance
GC	Gas Chromatography
HDS	Hydrodesulfurization
HPLC	High-Performance Liquid Chromatography
H	Hour
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
IEA	International Energy Agency
ISO	International Organization for Standardization
LOD	Limit of Detection
LOQ	Limit of Quantification
MAG	Monoacylglycerol
mL	Milli Liter
MS	Mass Spectrometer
nm	nanometer

NOx	Oxides of Nitrogen
ppm	Parts per million
rpm	Rotation Per Minute
SOx	Oxides of Sulfur
TAG	Triacylglycerol
TLC	Thin Layer Chromatography

1. Introduction

1.1. Project Background

The United Nations has made clean energy and environmental protection top priorities in its 2030 Sustainable Development Goals (SDGs) (Haruna *et al.*, 2022). Energy is essential for every aspect of socio-economic development worldwide. The global energy demand has been steadily rising, attributed to rapid urbanization, industrialization, and population growth (Tanimu *et al.*, 2019). The global population is expected to surpass 9 billion by the year 2050 (Neupane *et al.*, 2022). Over the period from 1990 to 2020, there was a notable surge in global energy consumption by 69.22%, paralleling with a 47.67% rise in the world's population. This increase in energy consumption has primarily been met by fossil fuels, which continue to dominate as primary energy sources (Chanthakett *et al.*, 2024). In 2018, coal, oil, and gas accounted for 85% of the total primary energy consumption (Kober *et al.*, 2020). However, reliance on fossil fuels poses sustainability challenges due to their limited supply and eventual exhaustion (P. Liu *et al.*, 2020). Additionally, rising crude oil prices, the irreversible decline in oil reserves, and escalating environmental degradation exacerbate these issues (Saifuddin *et al.*, 2009). The combustion of fossil fuels has led to notable environmental challenges due to the emission of greenhouse gases (COx, SOx, NOx), and these problems are expected to increase in the future (Correa *et al.*, 2019). Hence, there is an increasing call for alternative energy sources that are both environmentally friendly and sustainable (Krishnan *et al.*, 2021).

Renewable energy is an energy source that can be naturally replenished in a relatively brief timeframe. It can be generated through various methods and from diverse sources, including solar, wind, biomass, hydroelectricity, geothermal, tidal power, and more (Sattar *et al.*, 2020). Among these, a substantial portion of research in renewable energy is focused on harnessing the energy potential of biomass. Biomass is a versatile renewable energy source that can produce solid, gaseous, and liquid fuels suitable for various applications (Fang *et al.*, 2020). According to Asikin-Mijan *et al.* (2023), biomass can be categorized into two main types: solid and liquid. Solid biomass comprises agricultural crops and residues, forest products, animal waste, industrial by-products, and municipal solid waste. Liquid biomass includes vegetable oils, animal fats, and waste oils from cooking, food processing, and oil refining. Both types offer renewable energy alternatives that can help reduce dependence on fossil fuels and support sustainable energy practices (Duku *et al.*, 2011). Nonetheless, researchers have focused on using simple triacylglyceride forms of liquid biomass, like vegetable oils and animal fats, because converting solid biomass directly presents challenges and produces unwanted byproducts. In contrast, liquid biomass offers a less complex and more efficient process (Lidman Olsson *et al.*, 2023).

Biofuels refer to renewable and sustainable energy sources derived from natural biomass. These include solid fuels like pellets or briquettes used for combustion, liquid fuels such as biodiesel, bioethanol, and green diesel, and gaseous fuels like syngas (Asikin-Mijan *et al.*, 2023). Biofuels have emerged as a promising long-term energy solution with the potential to address environmental impacts and security concerns associated with current fossil fuel dependence (Alamu *et al.*, 2007; Batidzirai *et al.*, 2006). These fuels can enhance sustainability and significantly reduce carbon emissions, approximately 80–90% lower than fossil fuels. As a result, this makes them a compelling solution for addressing our energy needs while minimizing environmental impact (Kang *et al.*, 2019; Tham *et al.*, 2018; Y. Yang *et al.*, 2018).

In the realm of biomass sources, lipid feedstocks are particularly promising for generating renewable liquid hydrocarbons due to their higher energy density (Flores Luque *et al.*, 1986; Luque *et al.*, 1985) and simpler structure compared to alternatives like lignocellulose (Popov & Kumar, 2013). Plant oils, vegetable oils, microbial lipids, and animal fats are ideal feedstocks for biofuel production, as they are rich in storage lipids, primarily triacylglycerols (M. A. Peters *et al.*, 2022; J. Wang *et al.*, 2022). Triacylglycerol is a glycerol molecule connected to aliphatic carbon chains ranging from C6 to C24. These carbon chains can be saturated, monounsaturated, or polyunsaturated, depending on the presence and number of double bonds in their structure (M. A. Peters *et al.*, 2022). The hydrolysis of fats and oils, mainly triacylglycerols, produces fatty acids (Demirbas, 2008). Fatty acids are a group of organic acids that consist of saturated, straight-chain acids with a COOH carboxylic functional group. The fatty acid components in these lipids possess chemical properties, including carbon chain length, saturation level, and branching, that are largely comparable to those found in conventional fuels such as gasoline and diesel (J. Wang *et al.*, 2022). Moreover, Bezergianni *et al.* (2018) also state that fuel from lipids contains hydrocarbons, including n-alkanes and alkenes, similar to conventional petroleum diesel's composition.

Therefore, they are considered fully infrastructure-compatible fuels and can be utilized in engines without engine modification (Liao *et al.*, 2016; Othman *et al.*, 2017).

Among different methods, a two-step thermal conversion is a notable technique employed to transform lipid feedstocks into renewable fuels and chemicals (Asomaning *et al.*, 2014b). This process consists of two stages: the breakdown of lipids into free fatty acids through hydrolysis and the conversion of these acids into renewable hydrocarbons via pyrolysis through deoxygenation and thermal cracking (Asomaning *et al.*, 2014a). These products can be further refined into drop-in fuels, offering a way to turn lipid resources into high-value liquid products and promote sustainable energy solutions (Asomaning *et al.*, 2014b). In this study, diesel was the main product of the thermochemical conversion process. However, both the feedstocks and final products contain sulfur compounds, which present challenges due to their environmental, health, and operational effects.

Sulfur compounds are among the most frequently found impurities in transportation fuels. It can be found in different forms, including mercaptans, thiophene, disulfide, and sulfide (Chandra Srivastava, 2012). Subsequently, the emission of sulfur compounds during fuel combustion poses significant environmental challenges. When these substances enter the atmosphere, they can react with water vapor to create acidic rain and fog, which have the potential to cause damage to buildings, impact soil and forests, and disrupt the pH balance of water bodies, particularly oceans, leading to substantial disturbances in the ecosystem (Lelieveld *et al.*, 1997; Nehlsen, 2006; Song & Ma, 2003). A study by Stanislaus *et al.* (2010), found that sulfur compounds can produce particles that create black exhaust smoke. This smoke is notorious for its ability to penetrate the lungs deeply and pose significant health risks, such as asthma, chronic bronchitis, emphysema, as well as neurological problems (Han *et al.*, 2018). Therefore, this release can worsen air quality and negatively impact human health (Sydbom *et al.*, 2001). The sulfur compounds also accelerate pipeline and equipment corrosion (Tahir *et al.*, 2021), exacerbating environmental and economic concerns. In response, global authorities have imposed strict regulations, limiting diesel fuel sulfur content to around 15 ppm or less to reduce harmful emissions and enhance air quality (Zhu *et al.*, 2020). Consequently, research initiatives worldwide are actively committed to exploring methods for desulfurizing fuels.

To address this issue, the refining industry has developed and implemented numerous desulfurization methods. Desulfurization is a process used to remove sulfur compounds from different types of samples by employing a range of techniques such as hydrodesulfurization (Wu *et al.*, 2020; Zou *et al.*, 2020), catalytic oxidation (Al-Khodor *et al.*, 2020; Etemadi *et al.*, 2018), biological desulfurization (D. Yang *et al.*, 2015), membrane separation (Subhan *et al.*, 2018), adsorption (Paul *et al.*, 2015; Tang *et al.*, 2011), oxidative desulfurization (Quyen *et al.*, 2019) and ultrasound-assisted oxidative desulfurization (Mei *et al.*, 2003).

Hydrodesulfurization transforms sulfur compounds into hydrogen sulfide (H_2S) and sulfur dioxide (SO_2), which can be easily separated by using transition metal catalysts to remove stubborn sulfur compounds effectively (Haruna *et al.*, 2022). However, this process requires considerable expenses and energy consumption linked to the utilization of hydrogen under high temperatures and pressures (Ma *et al.*, 1994a; Vrinat, 1983) and compulsory catalytic system employment (Mochida & Choi, 2004). While effective in eliminating many aliphatic sulfur compounds like thiols, mercaptans, sulfides, and disulfide-containing impurities, hydrodesulfurization exhibits limited efficacy in completely removing persistent heterocyclic organosulfur compounds, such as thiophene (Królikowski *et al.*, 2013), benzothiophene (Al-Zahrani *et al.*, 2014), and dibenzothiophene compounds (Betiha *et al.*, 2018). This challenge arises from the structural and property similarities shared by the sulfur compounds with benzene fused-ring compounds, which are characterized by high thermal stability and chemical inertness (Ogunlaja *et al.*, 2014; Pouladi *et al.*, 2019). Therefore, alternative ultra-deep desulfurization processes are desired.

Oxidative desulfurization combined with extraction has received much attention as a promising technique for sulfur removal, offering several advantages such as mild reaction conditions, high selectivity, not requiring hydrogen, and economic viability (Campos-Martin *et al.*, 2010; Mjalli *et al.*, 2014). In the presence of an oxidant and suitable catalyst, this method converts refractory sulfur compounds into their polar derivatives, sulfoxide and/or hexavalent sulfone (Muhammad *et al.*, 2018; Mužic & Sertić-Bionda, 2013). These derivatives can then be easily separated from the oil through solvent extraction or adsorption (Campos-Martin *et al.*, 2010; Mjalli *et al.*, 2014; Mondal *et al.*, 2006). Integrating ultrasonic treatment into oxidative desulfurization processes presents an environmentally friendly approach, harnessing cavitation, mechanical action, and thermal processes for efficient desulfurization (Lin *et al.*, 2020). Hydrogen peroxide is the predominant oxidizing agent used in oxidative desulfurization. This is due to its high oxidation potential, high reactivity, and environmental compatibility (Ahmed *et al.*, 2023; Jiang *et al.*, 2009; Lü *et al.*, 2014; Ribeiro *et al.*, 2015). Hydrogen peroxide contains a large percentage of active oxygen by weight (47%) and decomposes into water and oxygen under mild conditions, minimizing the production of harmful by-products and adhering to the principles of green chemistry (Campos-Martin *et al.*, 2006; Ribeiro *et al.*, 2015; Tahir *et al.*, 2021; G. Yu *et al.*, 2005).

This research utilized four solvents: water, acetonitrile, methanol, and diethylene glycol mono ethyl ether. Acetonitrile, a polar aprotic solvent with no hydrogen bonding, possesses a high dielectric constant, enabling it to dissolve a range of ionic and nonpolar compounds (Alston Steiner & Gordy, 1966). Methanol is a polar protic solvent that can form hydrogen bonding. It is miscible with water and organic solvents, making it highly effective at dissolving a wide range of substances. Diethylene glycol mono ethyl ether possesses hydrophilic and hydrophobic properties, allowing it to dissolve diverse compounds.

In recent years, adsorptive desulfurization has garnered attention due to its cost-effectiveness, operational simplicity, and environmentally friendly nature, as it can be conducted under ambient temperature and pressure conditions (Fakhri, 2015; Fakhri *et al.*, 2017). Nonetheless, challenges persist in achieving ultra-low sulfur content of less than 15 ppm (Mguni *et al.*, 2019; Saleh, Sulaiman, Al-Hammadi, *et al.*, 2017). Clay materials, particularly bentonite, a montmorillonite clay with a 2:1 structure, hold significant promise as economical adsorbents (Choi *et al.*, 2017). Clay minerals are considered the most effective adsorbents due to their considerable specific surface area, pore volume, negative surface charge, and hydrophilic surface ((Srinivasan, 2011; Uddin, 2017)).

While thorough research and literature studies have examined desulfurization methods for conventional gasoline, diesel, and model fuels (which are intentionally contaminated with a known type and amount of sulfur), there is still limited information on removing sulfur compounds from actual biofuels (potentially containing different species of sulfur compounds) and their original sources or feedstocks. Furthermore, the existence of sulfur compounds in various chemical configurations makes their removal more challenging. With these in mind, (1) this study explored and assessed various desulfurization techniques such as solvent extraction, oxidation, ultrasonication, and adsorption to eliminate sulfur compounds from poultry fat, brown grease, and crude tall oils. (2) The study also investigated the sulfur removal during the thermochemical conversion of these non-edible lipid feedstocks into diesel equivalents. (3) Lastly, adsorptive desulfurization was examined for its effectiveness in removing sulfur from the produced diesel equivalents. The findings of this research aim to provide insights that could help reduce sulfur emissions for environmental protection while contributing to sustainable energy production.

1.2. Thesis Objectives

The overall objective of this research was to investigate the removal of sulfur compounds from poultry fat, brown grease, hardwood, and softwood tall oil soap via extraction, oxidation, ultrasonic-assisted oxidation, and adsorption techniques and throughout the conversion process of those feeds into renewable hydrocarbons.

The specific objectives were:

- To characterize the composition of poultry fat and brown grease, with a focus on sulfur content, as well as to extract and characterize crude tall oils from tall oil soap—a mixture of sodium/calcium salts and resin acids.
- To assess the efficiency of solvent extraction, oxidation, ultrasonication, and adsorption methods in removing sulfur compounds from feedstocks.
- To investigate the influence of operating parameters such as the temperature, catalyst-oxidant molar ratio, and catalyst-oxidant over feedstock concentration during oxidative desulfurization and to investigate the effect of acid activation and Fe III impregnation into bentonite clay on desulfurization.
- To explore the potential of clay, resin, and mesoporous adsorbent for desulfurizing feeds and diesel-equivalents derived from them.
- To assess the effectiveness of thermal hydrolysis, pyrolysis, caustic wash, and distillation processes in removing sulfur compounds during poultry fat and brown grease conversion into diesel equivalent.

1.3. General Experimental Hypothesis

A. Extractive desulfurization using solvents such as water, acetonitrile, methanol, and diethylene glycol mono ethyl ether will separate sulfur compounds from the sample due to the solvents' different polarities.

B. Oxidation of non-polar sulfur compounds using a mixture of hydrogen peroxide and acetic acid will convert them into hydro-soluble sulfones, facilitating their subsequent extraction using different solvents.

C. Ultrasonic-assisted oxidative desulfurization will facilitate the breakdown of complex sulfur compounds by activating reactive oxygen species through cavitation and by forming an emulsion to increase surface area. This will increase reaction rates and mass transfer and enhance contact. Hence, the resulting sulfones will be isolated using polar solvents.

D. Acid activation and introduction Fe^{3+} to bentonite clay will increase the specific surface area, porosity, and adsorption capacity. This is anticipated through impurity removal (e.g., carbons, sulfur), and cation exchange like K^{+}, Na^{+}, $\mathrm{Ca}^{2+}$with H^{+}ions, and leaching of Al^{3+} , Fe^{3+}, Mg^{2+} from the clay sheets.

E. Sulfur will be removed at various stages of the thermochemical conversion of poultry fat and brown grease into diesel-equivalent fuel through hydrolysis, pyrolysis, caustic wash, and distillation. The integrated processes are expected to break sulfur bonds, form sulfur radicals, and remove sulfur compounds.

2. Literature review

2.1. Biomass

Biomass refers to all organic material originating from plant, animal, and microbial sources. This includes resources such as wood and wood by-products, agricultural crops and their residues, municipal solid waste, animal manure, food processing by-products, and aquatic plants like algae (Demirbaş, 2001). Due to their economic and environmental importance, these biomass resources face various competing uses. Biomass can be harnessed to produce electricity, heat, and steam, as well as for generating transportation fuels. Additionally, it finds applications in the food processing, animal feed, and wood processing industries (Demirbaş, 2001).

Biomass has considerable potential to fulfill the growing demand for energy and raw materials while also helping to minimize environmental impact (Kajaste, 2014). According to a study conducted by Alper *et al.* (2020), biomass currently generated 5×10^{19} kJ of energy in 2020, representing approximately 10% of the global energy consumption. This figure is projected to surge to 150×10^{19} kJ by 2050, owing to the diverse array of available biomass resources. Unlike other alternatives, biomass has the unique capability of being directly converted into fuels and chemicals, offering versatility beyond conventional methods of electricity generation (Gnanasekaran *et al.*, 2023). Utilizing lignocellulosic biomass presents a challenge due to its high oxygen content (Cherubini, 2010). However, this issue could potentially be addressed by using feedstocks like fatty acids from algae (Chiaramonti *et al.*, 2017; Espinosa-Gonzalez, Asomaning, *et al.*, 2014), as well as inedible fats and oils (Atabani *et al.*, 2013).

2.2. Lipids

Lipids, often called fats and oils, are hydrophobic, water-insoluble substances in plants and animals. They consist mainly of three fatty acid molecules esterified to glycerol, commonly known as triacylglycerols (TAGs) (Sonntag, 1979). Typical neutral lipids include triacylglycerols (TAGs), diacylglycerols (DAGs), monoacylglycerols (MAGs), free fatty acids (FFAs), hydrocarbons, and various pigments (Manning, 2022). Lipid feedstocks are recognized as highly promising biomass sources for producing renewable liquid hydrocarbon products, offering viable alternatives to petroleum. Their superiority in energy density (Flores Luque *et al.*, 1986; Luque *et al.*, 1985) and uncomplicated structure (Popov & Kumar, 2013), in contrast to other biomass sources, such as lignocellulose, is the primary reason for this acknowledgment.

2.2.1. Non-edible Lipids

Non-edible lipids are lipids that are not meant for food consumption. This includes waste oils and animal fats, providing an alternative to food-based feedstocks (Asikin-Mijan *et al.*, 2023). Vegetable oils and animal fats primarily consist of triacylglycerols (TAGs), with monoacylglycerols, diacylglycerols, free fatty acids, sterols, and phospholipids present as minor components. Brown grease and yellow grease, waste oils, and fats exhibit elevated levels of these minor components, specifically free fatty acids, compared to virgin or refined oils and fats (Fan *et al.*, 2013; Sari *et al.*, 2013; Ward, 2012). Furthermore, non-edible plant oils, which are widely available, also offer high productivity and yield. Additionally, their growth is not heavily dependent on regional weather conditions, making them easy to cultivate with minimal care and lower cost (Asikin-Mijan *et al.*, 2023).

Various lipid feedstocks have been investigated as inputs for producing free fatty acids via thermal hydrolysis. These feedstocks include oleaginous yeast and microalgae (Espinosa-Gonzalez, *et al.*, 2014; Espinosa-Gonzalez, 2014). Oleaginous microorganisms can store up to 70% of their dry cell mass as lipids, making them excellent candidates for biofuel production (Papanikolaou & Aggelis, 2011). Particularly, some oleaginous microalgae are recognized for their high photosynthetic efficiency, fast growth rates, and ability to accumulate large quantities of lipids under stress conditions, positioning them as prime sources for lipid-based biofuel production (J. Wang *et al.*, 2022). The utilization of diversified non-edible feedstocks for fuel production is essential, as it mitigates the risk of scarcity associated with any singular source and confronts challenges related to land availability, biodiversity loss, and price volatility resulting from crop failures (Kargbo *et al.*, 2021). Based on these reasons, this study utilized non-lipid feedstocks such as poultry fat, brown grease, and tall oils, which will be discussed in the next section.

2.2.1.1. Poultry Fat

Poultry fat is primarily derived as a byproduct from the rendering process of chicken, turkey, and other birds. It primarily contains oleic acid as its monounsaturated fatty acid and linoleic acid as polyunsaturated fatty acid (Sohail *et al.*, 2022). These unsaturated fatty acids are highly susceptible to oxidation (Bravo-Lamas *et al.*, 2018). Oleic acid, constituting nearly 40% of the fatty acids in poultry fat, has been extensively studied for second-generation biofuel production (Kirubakaran & Arul Mozhi Selvan, 2018). Hydrocracking poultry fat with a nickel-tungsten catalyst can yield 80% renewable hydrocarbons, including 40% gasoline-equivalent and 30% diesel-equivalent (Hanafi *et al.*, 2016). Additionally, chicken carcasses, containing about 40% crude fat, have been processed through hydrothermal and microwave treatments to produce bio-oil, highlighting the potential of converting poultry waste directly into biofuels (Zhang *et al.*, 2020). According to Sohail *et al.* (2022), sulfur-containing compounds in poultry encompass various thiols, sulfides, thiophenes, and thiazoles. Key thiols include methanethiols and 2-furfurylthiol, while notable sulfides are dimethyl disulfide, 2-methyl-3-(methylthio)furan, and methional. Thiophenes such as 2-methyl thiophene and 2-thiophene carboxaldehyde are also present. Additionally, the group includes thiazoles like 4-methylthiazole, 4-methyl-5-hydroxyethyl thiazole, and benzothiazole.

2.2.1.2. Brown Grease

Brown grease or grease trap is the lipid component obtained from a mixture of food particles and other substances commonly found in kitchens, commercial food preparation sites, or wastewater treatment facilities (Ward, 2012). It is recognized for its high energy content, estimated to be around 12,000 British Thermal Units (BTU) per pound (Sari *et al.*, 2013). Additionally, waste oils, such as used frying oils and brown grease, are inexpensive lipid materials and valuable resources for cost-effective feedstock options compared to food-grade vegetable oils. (Canakci & Van Gerpen, 2003; Knothe *et al.*, 2005). Waste cooking oil or waste fryer grease is classified based on its free fatty acid (FFA) content. If the FFA content of the waste cooking oil is less than 15% it is referred to as “yellow grease”; otherwise, it is termed “brown grease” (M. Canakci & J. Van Gerpen, 2001). Brown grease, known for its high water and free fatty acid content, is frequently disposed of through landfilling or combustion, resulting in significant loss of potential feedstock and revenue opportunities (Spiller *et al.*, 2020). Some brown grease undergoes anaerobic digestion to produce biogas despite encountering operational hurdles like incomplete conversion, sludge flotation, foaming, and system blockages (Long *et al.*, 2012).

Frying is a widely practiced cooking method in modern kitchens (Gazmuri & Bouchon, 2009). After frying, fats and oils undergo several noticeable physical transformations, including increased free fatty acid (FFA) levels, change in oil color to dark brown or red, changes in surface tension, higher viscosity, and specific heat (Cvengroš & Cvengrošová, 2004). Studies conducted by Nawar (1984) and Mittelbach & Enzelsberger (1999) on frying oil indicate that three main type of reactions occur during the frying process: thermolytic, oxidative, and hydrolytic.

A. Thermolytic reactions occur at high temperatures without oxygen, producing normal alkanes, alkenes, lower fatty acids, and other compounds from saturated fatty acids.
B. Oxidative reactions involve the reaction of unsaturated fatty acids with oxygen, forming hydroperoxides and various decomposition products.
C. Hydrolytic reactions occur due to steam during food preparation, causing the breakdown of triacylglycerides into free fatty acids, glycerol, monoglycerides, and diglycerides. The increase in oil's polar content upon repetitive heating serves as an indicator of oil quality, with European countries establishing a maximum polar content level of 25% for edible oils. Studies demonstrate a significant rise in polar content after multiple frying, indicating oil degradation. The addition of fresh oil during frying can partially alleviate these changes.

2.2.1.3. Tall Oil Soap

Tall oil is a by-product of the kraft or sulfate process for wood pulping (Demirbas, 2008). It comes from woody biomass grown on land unsuitable for farming and not meant for consumption (Vevere *et al.*, 2020). Annually, around 1.6 to 2 million tonnes of crude tall oil are generated (D. Peters & Stojcheva, 2017). Tall oil consists of saponified fatty acids (30-60% by mass), resin acids (40-60% by mass, mainly abietic and pimaric acids), and unsaponifiables (5-10% by mass) originating from softwood extractives (Uusi-Kyyny *et al.*, 2017). Aro & Fatehi, (2017), state that terpenes, fatty and resin acids, sterols, and alkane extractives are frequently not fully utilized during pulping. These components typically comprise about 1-8 wt.% of oak and willow hardwoods, while pine, classified as a softwood, can contain as much as 10 wt.% of extractives. The composition of tall oil varies based on factors such as the type and age of the tree, geographic location, season of harvest, and the conditions under which the feed wood is stored and pulped (Aro & Fatehi, 2017; Aryan *et al.*, 2019; Niemi *et al.*, 2016). Demirbas, (2008), mentioned that the fatty acids derived from tall oil have the potential to be utilized as a raw material for biodiesel production. Employing tall oil to produce chemicals and fuels does not threaten food security, given that it is a non-consumable resource.

In the kraft process, the raw wood is reduced to chips, which are then digested under heat and pressure with a solution mixture of sodium hydroxide, sodium sulfide, and minor sodium salts such as sodium carbonate and sodium thiosulfate. This dissolves triacylglycerides and resin acids for delignification (Wool & Sun, 2005). The cooking process generates a byproduct called black liquor, containing lignin, hemicellulose, and various inorganic chemicals used in the pulping process. The black liquor is a sticky, dark brown liquid with an unpleasant odor (Fengel D. & Wegener G., 1983). It is acidified and partially concentrated to isolate crude tall oil (CTO) via evaporation and skimming, as tall oil soap has a lower density than black liquor. This technique separates 40-80% of tall oil soap from black liquor while the remaining tall oil components remain dissolved in the black liquor (Churchill *et al.*, 2024). The tall oil soap is then treated with sulfuric acid to convert sodium soap into free resin and fatty acids (Fengel D. & Wegener G., 1983). As stated by Aro & Fatehi, (2017), approximately 20-40% of tall oil soap is classified as waste. Possible applications of this waste include using it as fuel for generating energy during paper production or refining it to create crude tall oils. Utilizing sulfur-containing compounds during the Kraft process produces a strong foul odor. This poses a risk of introducing harmful sulfur contaminants into tall oil products, making them less environmentally friendly (Cheremisinoff & Rosenfeld, 2010).

Tall oil soap in black liquor causes major problems in the Kraft process, such as scaling in the evaporators, decreasing heat transfer efficiency, and ultimately reducing overall pulp production (Uloth & Wong, 1986). The combustion of tall oil soap in a recovery boiler leads to higher sulfur emissions, reduced boiler efficiency, faster fouling, and more complex process control (Aro & Fatehi, 2017). Furthermore, the resin acid components in the tall oil soap increase the toxicity of Kraft mill wastewater (Drew, 1981; Hutchins, 1979). Resin acids mainly include abietic, levopimaric, neoabietic, and dehydroabietic acids. They typically possess conjugated double bonds, which contribute to their high reactivity in terms of chemical properties. More specifically, levopimaric acid and neoabietic acid have conjugated double bonds, while dehydroabietic acid is an aromatic compound with stable chemical properties (P. Liu *et al.*, 2020).

Given the issues caused by tall oil soaps in the Kraft process, it is important to explore alternative applications for them. One possible solution is to convert them into crude tall oils without using sulfuric acid. These crude tall oils possess a substantial calorific value, with a heating value of 37.9 MJ/kg, making them suitable for utilization and processing in energy production (Adewale *et al.*, 2017). Additionally, removing the sulfur from these crude tall oils could enhance their value. Therefore, this research will investigate these possibilities.

2.3. Biofuels

Biofuels refer to renewable and sustainable energy sources derived from natural biomass (Asikin-Mijan *et al.*, 2023). These include lignocellulosic substances, oleaginous plants or microbes, lipids of animal fats, and municipal organic wastes (Abomohra *et al.*, 2020). Given the risks associated with global climate change and the depletion of oil reserves, there is a growing interest in the research and development of biofuels (Rogers & Zheng, 2016). Demand for biofuels is projected to grow by 38 billion liters between 2023 and 2028, marking a nearly 30% increase compared to the previous five years (IEA, 2024). Various biofuels exist, including biodiesel, crude bio-oil, bioethanol, biogas, biohydrogen, and green diesel (Asikin-Mijan *et al.*, 2023). Liquid biofuels are particularly appealing due to their compatibility with conventional engine infrastructures (Abomohra *et al.*, 2020).

2.3.1. Green Diesel

Green diesel, also called renewable diesel, is a liquid biofuel. It offers an oxygen-free liquid hydrocarbon fuel compatible with conventional diesel engines (Hossain *et al.*, 2018). It contains short-chain hydrocarbons with carbon lengths from C6 to C12, resembling those found in gasoline and long-chain hydrocarbons with carbon lengths from C13 to C20, similar to those in diesel. Mainly composed of n-alkanes and n-alkenes, green diesel closely resembles the chemical structure of gasoline and diesel produced in traditional petroleum refineries (Asikin-Mijan *et al.*, 2023). Green diesel has a higher heating value, greater energy density, and a remarkably high cetane number, surpassing biodiesel (Kalnes *et al.*, 2007; Orozco *et al.*, 2017). Unlike biodiesel, which varies significantly in fuel properties based on its feedstock and production process, green diesel remains consistent regardless of the feedstock used.

2.3.2. Biofuel Generations

Biofuels are categorized into different generations based on their source materials and production methods. Each generation employs different technologies, which results in distinct end products. This is due to the unique properties of the feedstock and the varying operational parameters (Bhaskar & Pandey, 2015).

2.3.2.1. First-Generation Biofuels

First-generation biofuels are fuels made from edible crops, causing a conflict between their use for food versus fuel (Bhaskar & Pandey, 2015). First-generation biofuels can be produced through transesterification, which chemically converts oils from vegetable and animal sources into biodiesel. A second approach involved the conversion of starches and sugars into alcohols such as bioethanol or butanol through fermentation (Cuellar-Bermudez *et al.*, 2015; Nigam & Singh, 2011). The feedstocks generally comprise agricultural products such as wheat, sugarcane, maize, nuts, and vegetable oils. Despite their demonstrated reduction in greenhouse gas emissions, first-generation biofuels have several drawbacks. These include competition with food crops, reliance on non-sustainable fertilizers hindering greenhouse gas reduction efforts, promotion of deforestation for agricultural expansion leading to biodiversity loss, and competition for clean water resources (R. A. Lee & Lavoie, 2013; Naik *et al.*, 2010; M. Naqvi & Yan, 2015). However, biodiesel is regarded as a viable alternative to petroleum diesel due to its favorable cetane number, lubricity, biodegradability, and nontoxicity (Ajala *et al.*, 2015). Unfortunately, due to the oxygen in its molecular structure, it also faces challenges such as chemical instability, poor cold flow properties, lower calorific value, engine compatibility issues, and filterability problems like hazes (Knothe, 2010; Santillan-Jimenez *et al.*, 2013).

2.3.2.2. Second-Generation Biofuels

Second-generation biofuels are sourced from non-edible materials (Bhaskar & Pandey, 2015). They involve agricultural waste (e.g., husks), non-food crops (e.g., elephant grass), and industrial waste (e.g., sawdust), which are typically disposed of in landfills or incinerated after extracting their valuable components (Czekała *et al.*, 2018; Danquah *et al.*, 2018; Guerrero & Muñoz, 2018;

Hu *et al.*, 2018). Forecasts indicate that second-generation biofuels will eventually significantly reduce costs and increase productivity efficiency. Positioned as a crucial element in transitioning the transportation sector toward sustainable and eco-friendly sources, they stand to benefit from ongoing technological advancements and fluctuations in fossil fuel prices (Hassan *et al.*, 2018; Santamaría & Azqueta, 2015). Nonetheless, challenges persist in their production, including biomass complexity and issues associated with production, transportation, harvesting, and pretreatment before biofuel manufacture (Kargbo *et al.*, 2021).

2.3.2.3. Advanced Biofuels

Advanced biofuels are produced from aquatic biomass, such as algae (Bhaskar & Pandey, 2015). Interest in algae has surged because of their ability to convert sunlight and carbon dioxide into lipids and other carbon-rich biopolymers through photosynthesis (Milliren *et al.*, 2013). In lipid-rich algae, the energy is stored as triacylglycerides, much like fats found in vegetable oils and animal products (Milliren *et al.*, 2013). Algae offers several advantages over traditional terrestrial biomass sources, including a remarkable increase in growth rate, minimal land usage, and reduced need for fertilizers and pesticides. Moreover, the ability to use waste sources as nutrients and being unaffected by seasonal variation makes them more favorable (Dahman *et al.*, 2019; Lam *et al.*, 2019; Lazar *et al.*, 2019). However, the primary challenge with algae as a feedstock lies in the separation of water from the biomass, as algae cells consist of over 60-90% water (Xu *et al.*, 2011). Therefore, the costs and energy demands associated with fully dewatering and drying are substantial. According to Minami & Saka, (2006) and Levine *et al.* (2010), a practical approach to solving this problem is to use the water from harvested and partially dewatered algae to hydrolyze the lipids into free fatty acids. This method creates distinct aqueous and oil-rich phases, simplifying the extraction and separation of lipid components. The free fatty acids can then be converted into biofuels through deoxygenation. The cultivation of this type of biofuel biomass helps maintain environmental balance by consuming carbon dioxide from the atmosphere (Richmond, 2004). Similarly, oleaginous microorganisms, such as bacteria, fungi, and microalgae, are excellent candidates for biofuel production, as they can accumulate up to 70% of their dry cell weight in lipids (J. Wang *et al.*, 2022). Another advanced biofuel type involves genetically engineered plants and microorganisms (Bhaskar & Pandey, 2015). Additionally, the metabolic engineering of algae and plants increases biomass yields and improves feedstock quality while fixing carbon dioxide (Naveed *et al.*, 2023).

2.3.3. Biofuel Production Techniques

Various technologies are available for transforming biomass into fuels and chemicals; the most common methods include thermochemical conversion, direct combustion, physical extraction, biochemical conversion, electrochemical conversion, and indirect liquefaction (Prabir Basu, 2010). Biochemical conversion encompasses biodiesel production, anaerobic digestion, and ethanol synthesis. Indirect liquefaction involves Fischer-Tropsch synthesis. The selection of these processes is based on the characteristics of the feedstock. It can be moisture content, calorific value, proportions of fixed carbon, oxygen, hydrogen, nitrogen, volatiles, ash content, and cellulose/lignin ratios (Duku *et al.*, 2011). Among these methods, thermochemical routes are often regarded as the most viable options for biomass conversion (Prabir Basu, 2010).

2.3.3.1. Thermochemical Conversion Technologies

The conversion of fats and oils has traditionally centered on producing fatty acid alkyl esters, typically methyl esters, commonly known as biodiesel. Another viable approach is thermochemical conversion. The common thermochemical technologies include pyrolysis, hydrothermal liquefaction, gasification, and combustion (Mishra *et al.*, 2024). According to Bhaskar & Pandey, (2015), pyrolysis is a process that involves heating materials in the absence of oxygen, leading to the breakdown of organic matter into various products. Hydrothermal liquefaction involves reactions in the presence of water or a solvent, resulting in the production of bio-oil (such as fuels, chemicals), biochar (like catalyst or catalyst support, adsorbent, fertilizers) and gases (like hydrogen). Gasification is a method that involves partial oxidation, producing syngas. Lastly, combustion occurs when a substance is heated in the presence of oxygen, releasing energy and other byproducts. Among these, pyrolysis is highly favored due to its relative simplicity and ability to produce solid, liquid, and gaseous fuels (Jahirul *et al.*, 2012; Mishra *et al.*, 2024). In addition, pyrolysis's ability to produce liquid fuels has garnered significant attention. These liquid fuels are easier to store, transport, and use in various applications such as combustion engines, boilers, and turbines. Furthermore, managing solid biomass and waste is often challenging and expensive, further driving research into pyrolysis (Jahirul *et al.*, 2012).

2.3.3.1.1. Hydrolysis Process

Hydrolysis is typically the primary step in breaking down the triacylglyceride structure into free fatty acids and glycerol, which are fundamental for producing various end-user products (M. A. Peters *et al.*, 2022). Stoichiometrically, hydrolysis of triacylglyceride requires 3 moles of water to cleave the tri-ester bonds in 1 mole of triacylglyceride. Hence, 3 moles of free fatty acids and 1 mole of glycerol will be formed. Since the reaction is reversible, excess water is used to push the reaction equilibrium toward completion to ensure high conversion rates (M. A. Peters *et al.*, 2022). This process requires a substantial amount of water but not more than the volume of the feed. In addition, it also necessitates the use of compressed hot water at elevated temperatures, often termed superheated water or subcritical water, to ensure efficient oil conversion (H & McClain, 1949; Lascaray, 1952). Hydrolysis under high pressure is favored because it eliminates the need for a catalyst, which could necessitate extra steps for its removal, regeneration, and recovery.

Subcritical water is water in its liquid state at temperatures between 100 °C (its boiling point) and 374 °C (its critical point) (Toralles *et al.*, 2015). Subcritical water works well as a solvent for polar and non-polar compounds due to its adjustable polarity, which varies with temperature. When water temperature rises, its polarity decreases. Consequently, non-polar organics become more soluble, while polar organics become less soluble (Fernández-Prini *et al.*, 1991). The dielectric constant value is used to measure the polarity of subcritical water (Carr *et al.*, 2011).

Hydrolyzing triacylglycerides in subcritical water, typically at temperatures ranging from 200 to 370 °C and pressures below 22.1 MPa, represents an autocatalytic process (Toralles *et al.*, 2015; Yulianto *et al.*, 2020). In subcritical water, a high concentration of hydrogen ions (H+) and hydroxide ions (OH-) that act as efficient catalysts. These conditions can weaken hydrogen bonds, lower the dielectric constant, and increase the ionic product (kW). As a result, these conditions promote the generation of hydrogen ions as acid catalysts and hydroxide ions as base catalysts (Ruiz *et al.*, 2013). The unique characteristics of hot-pressurized water allow it to act as a reaction medium, reactant, and catalyst for organic reactions. This makes it particularly effective for the rapid hydrolysis of oils and fats into fatty acids and glycerol (Savage, 1999).

2.3.3.1.2. Pyrolysis Process

Pyrolysis, or thermal cracking, is a thermochemical conversion process that transforms free fatty acids into liquid products and non-condensable gases while producing solid “coke” as an undesirable by-product (Yaman, 2004). It is characterized by thermal decomposition without oxygen, leading to varied outcomes influenced by temperature and vapor residence time (Yogalakshmi *et al.*, 2022). Lower temperatures and extended vapor residence favor charcoal production, whereas higher temperatures and longer residence times promote gas conversion from biomass. Optimal conditions for liquid production involve moderate temperatures and shorter vapor residence periods. Pyrolysis yields a high fuel-to-feed ratio when applied to lipid conversions. Hence, it is one of the most efficient and promising technologies in lipid conversion, with the potential to compete directly with petroleum-based fuels (Aresta *et al.*, 2012; Demiral *et al.*, 2012; Şensöz & Can, 2002). Based on the research conducted by Wisniewski *et al.* (2010), bio-oils derived from triacylglyceride materials predominantly consist of alkanes, alkenes, ketones, aldehydes, aromatics, and carboxylic acids. Conversely, those produced from lignocellulosic biomass primarily comprise phenols, furans, and their derivatives. This technology presents notable benefits compared to transesterification, including reduced processing expenses, alignment with existing infrastructure, engines, and fuel standards, as well as versatility in feedstock options (Stumborg *et al.*, 1996). Moreover, pyrolysis offers benefits in terms of its simplicity and affordability in construction (Onay & Koçkar, 2004).

2.3.3.1.2.1. Deoxygenation

Several conversion technologies have been developed to transform highly oxygenated natural lipid biomass, like triacylglycerides and fatty acid derivatives, into diesel-like hydrocarbons. These methods include catalytic cracking (H. Wang *et al.*, 2019; Zhao *et al.*, 2015), hydrotreating (Elkasabi *et al.*, 2014), and deoxygenation (S. R. Naqvi *et al.*, 2023; Smoljan *et al.*, 2020). Among these, the deoxygenation process is both economically viable and efficient for producing diesel-like hydrocarbons, known as green diesel (Asikin-Mijan *et al.*, 2023). This process can be conducted under a hydrogen flow, termed hydrodeoxygenation, or in a hydrogen-free environment. Utilizing hydrogen supports the thermodynamically preferred hydrogenation pathway (Žula *et al.*, 2022). However, while hydrogen can reduce catalyst deactivation rates compared to inert atmospheres, its practical and economic feasibility is constrained by its high consumption rate

(Asikin-Mijan *et al.*, 2023). The expense of hydrogen and the energy required for its production significantly affects the cost of deoxygenation processes. Additionally, hydrogen's highly flammable nature demands stringent safety measures and additional infrastructure, complicating workflows and increasing costs. Large-scale hydrogen production from renewable sources is still developing, and issues related to availability and cost-efficiency may be faced (Žula *et al.*, 2022). Deoxygenation can proceed through two main pathways: decarbonylation, which eliminates the carbonyl group (C=O) as both water and CO, resulting in alkanes or alkenes with one fewer carbon atom than the original fatty acid, and decarboxylation, which removes carboxyl group (-COOH) as CO_2, producing alkanes with one less carbon unit (Aslam *et al.*, 2022; Santillan-Jimenez & Crocker, 2012).

2.3.3.1.2.2. Catalytic Pyrolysis

Catalytic pyrolysis refers to the pyrolysis process that is carried out in the presence of catalysts (Chen *et al.*, 2024). Biomass pyrolysis can be conducted using various catalysts, including sodium hydroxide, metal salts, zeolites, metal oxides, and carbon-based catalysts. Each of these catalysts possesses distinct characteristics and impacts the pyrolysis process in different ways (Sankaranarayanan & Won, 2024). The choice of catalyst is crucial in biomass pyrolysis, as it ideally needs to meet criteria such as being cost-effective, highly active and selective, resistant to deactivation, and easily recyclable. In catalytic pyrolysis, the catalyst can be introduced either by mixing it directly with the biomass (in-situ method) or by interacting solely with the vapors produced during pyrolysis (ex-situ method) (Yildiz *et al.*, 2013). The catalytic pyrolysis method offers several advantages over non-catalytic pyrolysis, including a reduction in pyrolysis temperature by lowering the activation energy, shortening the reaction time, and improving selectivity for desired liquid products (Hafeez *et al.*, 2019). Additionally, it allows for better control over the distribution of hydrocarbon products, resulting in a narrower and more targeted range of outputs (Hafeez *et al.*, 2019).

Catalytic deoxygenation/pyrolysis is an effective method for lowering the oxygen content in bio-oil. According to Wang *et al.* (2017), this process typically involves reactions such as dehydration, decarboxylation, and decarbonylation, which remove oxygen as H_2O, CO_2, and CO, respectively. Catalytic cracking is employed to break down large molecules and heavy organic compounds into smaller products. During this process, oxygenates are also converted into aromatics and olefins.

The catalytic cracking process involves various reactions, including C-C bond cleavage, hydrogen transfer, isomerization, aromatic side-chain scission, and deoxygenation. Aromatization is another key process that converts low-molecular-weight oxygenates and olefins into aromatics. Additionally, ketonization transforms two carboxylic acid molecules into a ketone, CO_2, and H_2O. This reaction not only removes carboxyl groups but also facilitates C-C coupling without the need for external hydrogen, enhancing the heating value and stability of the final products.

2.3.3.1.3. Distillation Process

The process of separating mixtures based on differences in the volatility of individual components is known as distillation. It is a widely applied technique in the chemical and petroleum industries. Distillation has been employed to separate pyrolytic liquid fractions. Some of these fractions can be upgraded to meet fuel requirements, while others can be used for chemical production (W. Li *et al.*, 2011; Mancio *et al.*, 2018). This method helps isolate volatile compounds in the pyrolytic liquid that affect its fuel characteristics. Successful separation by distillation requires a sufficiently large relative volatility between the components.

2.4. Global and Regional Sulfur Regulations Overview

In 1970, the Environmental Protection Agency (EPA) implemented the Clean Air Act in response to growing concerns about environmental protection and public health (Ross *et al.*, 2012). Moreover, regulatory bodies are increasingly implementing strict regulations to reduce the high sulfur content of transportation fuels to very low levels. The USA, Europe, and Japan are tightening gasoline and diesel fuel sulfur content limits. For instance, in the USA, the permissible level of sulfur in diesel has undergone successive reductions mandated by the Clean Air Act amendments: from 500 ppm in 1995 to 350 ppm in 2000, then to 50 ppm in 2005, and ultimately to 15 ppm since 2010. Similarly, in the European Union, the maximum sulfur content allowed in market diesel was reduced to 10 ppm as of 2010 (Ali *et al.*, 2006; Jeon *et al.*, 2009; Kim *et al.*, 2006; Song, 2003; Song & Ma, 2003). Germany imposed a 10 ppm sulfur concentration limit on gasoline and diesel fuels in 2001. China followed, adopting the same 10 ppm limit in late 2017 (Shafiq *et al.*, 2022).

The Canadian General Standards Board (CGSB) has set stringent specifications for automotive gasoline, diesel, and jet turbine fuel to regulate sulfur content, ensuring environmental protection and public health. The standard for automotive gasoline (CGSB-3.5-2021) mandates a maximum sulfur content of 80 ppm. This limitation aims to curb harmful vehicle emissions, aligning with environmental regulations and promoting cleaner air quality. Similarly, diesel fuel (CGSB-3.517-2020) is subject to a sulfur content cap of 15 ppm. By reducing sulfur in diesel, the standard seeks to mitigate diesel exhaust emissions, including sulfur dioxide and particulate matter, which pose health risks and contribute to air pollution. The standard for jet turbine fuel (CGSB 3.23-2023) dictates a sulfur content not exceeding 0.30% by mass (3000 ppm). This specification ensures safe and efficient aircraft engine operation while minimizing environmental impact. Compliance with these CGSB standards is essential for industry stakeholders to uphold environmental responsibility, meet regulatory requirements, and contribute to sustainable transportation practices in Canada.

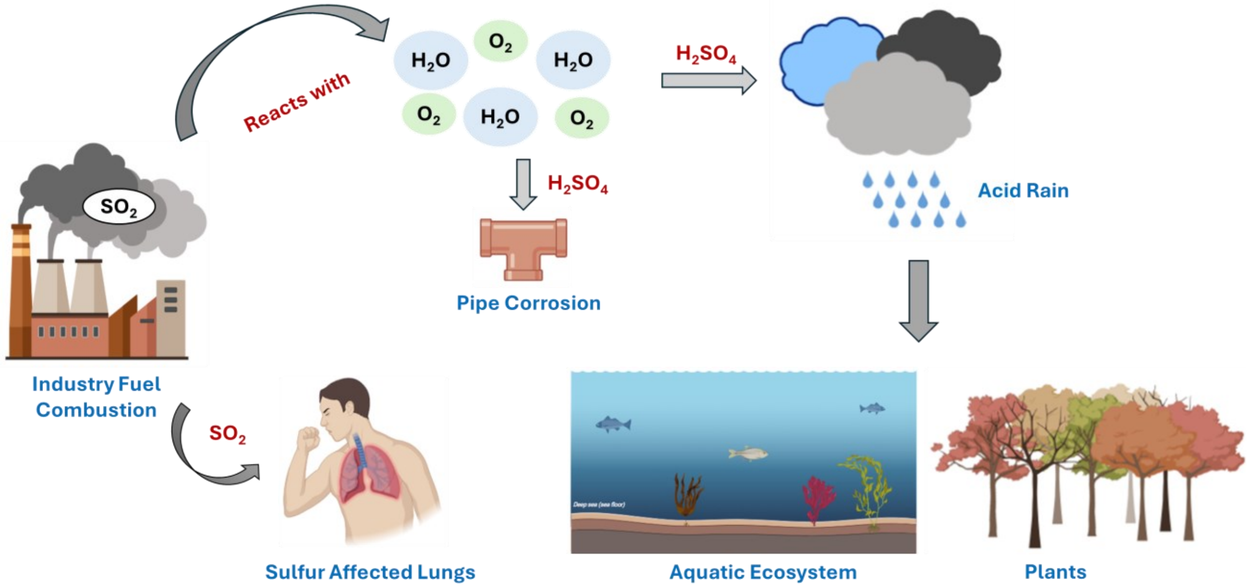


Figure 2.1. Simplified Graphical Representation of Environmental, Health, and Infrastructure Impacts of Sulfur

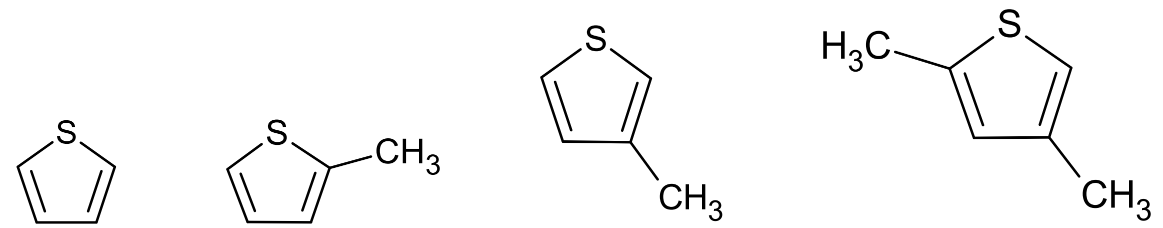
(Han *et al.*, 2018; Tahir *et al.*, 2021; Yadav *et al.*, 2021).

2.5. Sulfur Compounds Present in Transportation Fuels

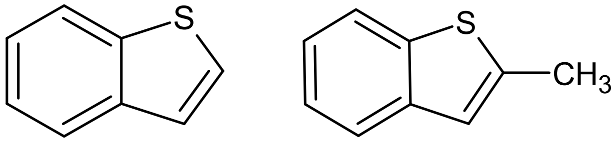
Sulfur compounds are categorized into organic and inorganic groups. The organic group includes thiols, sulfides, and thiophene compounds, while the inorganic group comprises elemental sulfur, hydrogen sulfide, and pyrites. (Agarwal & Sharma, 2010). Liquid fuels such as gasoline, jet fuel, and diesel are categorized based on their boiling ranges during refining. Lighter distillates typically contain mercaptans, sulfides, and disulfides, whereas middle distillates primarily comprise benzothiophenes and their alkylated derivatives (Harrop & Mascharak, 2004; Kobayashi *et al.*, 1992). Heavier distillates contain more heterocyclic aromatic sulfur compounds (Kovacs, 2004). Dibenzothiophene (DBT) and its derivatives are the major contaminants in diesel streams (Fox, 2011). Based on Mjalli *et al.* (2014) findings, the order of reactivity of sulfur compounds is sulfides > mercaptans > thiophenes > benzothiophenes > dibenzothiophenes > 4-methyl dibenzothiophenes > 4,6-dimethyl dibenzothiophenes. The sulfur atom's reactivity is influenced by both the surrounding environment and the molecule's overall structure (Shafi & Hutchings, 2000). The following are the prevalent types of sulfur compounds commonly found in liquid fuels, as Ma *et al.* (2002) identified.

a) Gasoline

Gasoline, the primary fuel for cars, is a lighter fraction of oil with a boiling point range of 25-225°C (Clemons, 2009). These sulfur compounds have relatively low steric hindrance compared to those in heavier liquid fuels. Thiophene, 2-methyl thiophene, 3-methyl thiophene, 2,4-dimethyl thiophene, benzothiophene, and 2-methyl benzothiophene are among the most abundant sulfur compounds in gasoline. As steric hindrance increases, removing these sulfur compounds becomes more challenging using conventional methods (Ma *et al.*, 2005).



Thiophene 2-Methylthiophene 3-Methylthiophene 2,4-Dimethylthiophene

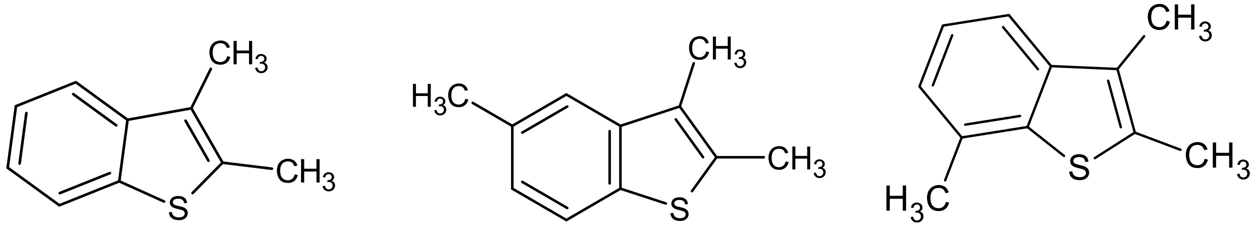


Benzothiophene 2-Methylbenzothiophene

Figure 2.2. Sulfur-containing compounds in Gasoline

b) Jet Fuel

Jet fuel typically boils within the 130-300°C range, and the sulfur content is predominantly composed of aromatic sulfur compounds (Clemons, 2009). Most of them are substituted benzothiophenes, such as 2,3-dimethyl-benzothiophene, 2,3,5-trimethyl benzothiophene, and 2,3,7-trimethyl benzothiophene. All these methyl benzothiophenes have two methyl groups positioned at the 2—and 3-positions, suggesting that benzothiophenes with two methyl groups at these positions demonstrate greater resistance to reduction compared to their counterparts in gasoline due to their heightened chemical stability (Velu *et al.*, 2003).

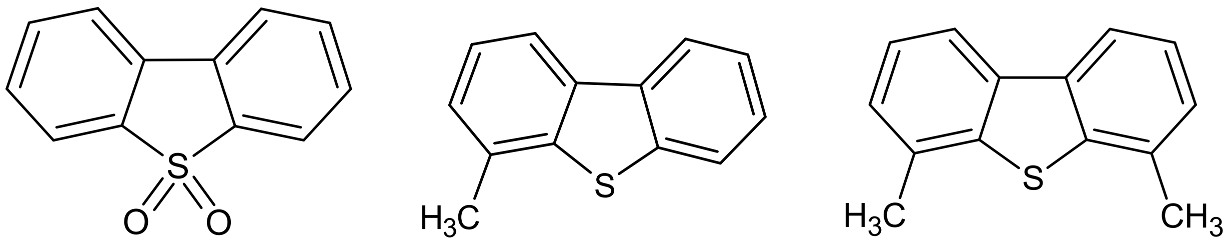


2,3-dimethyl-benzothiophene 2,3,5-trimethyl-benzothiophene 2,3,7-trimethyl-benzothiophene

Figure 2.3. Sulfur-containing compounds in Jet Fuel

c) Diesel Fuel

Diesel is widely utilized as a fuel in various modes of transportation, including highway vehicles like tracks, cars, and buses and non-highway systems like farm equipment, locomotives, and marine vessels. According to Mascal & Dutta, (2020), diesel fuel is a blend of hydrocarbon molecules with carbon chain lengths ranging from C_{14} to C_{20}, primarily consisting of straight-chain and branched alkanes. Diesel engines use 25-40% less fuel than equivalent gasoline engines. However, they experience detrimental particulate, nitrogen oxide, and sulfur oxide emissions that harm human health (Stanislaus *et al.*, 2010). It also offers a higher energy density than gasoline and has a boiling point range of 160-380°C (Clemons, 2009). Commercial diesel fuel contains sulfur compounds such as alkyl benzothiophenes and alkyl dibenzothiophenes, predominantly 4-MDBT, 4,6-DMDBT, 3,6-DMDBT, and 2,4,6-TMDBT. The alkyl groups are located at the 4- and/or 6-positions (Hernández-Maldonado & Yang, 2004). This suggests that the primary sulfur compounds remaining in diesel fuel are refractory. The sulfur compounds in diesel are notably heavier and have higher boiling points. With increasing molecular size, removing them using traditional sulfur removal techniques like hydrodesulfurization becomes progressively challenging. Their stubborn nature can be attributed to the methyl groups surrounding the sulfur atom, which create a steric effect (Hernández-Maldonado & Yang, 2004).



Dibenzothiophene 4-methyl-dibenzothiophene 4,6-dimethyl-dibenzothiophene

Figure 2.4. Sulfur-containing compounds in Diesel Fuel

2.6. ICP-OES Working Principle

Sulfur analysis involves various methods of detecting, quantifying, and identifying the presence of sulfur in a sample. Accurate sulfur analysis is crucial for ensuring compliance with environmental regulations, maintaining product quality, and ensuring the safety of operations. This analytical technique is important in various industries, including petrochemicals, energy, mining, and pharmaceuticals. Several methods of sulfur analysis are applied, each offering unique advantages and limitations. The most common methods include X-ray fluorescence, ultraviolet fluorescence spectroscopy, and inductively coupled plasma optical emission spectrometry.

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) is an analytical technique used to determine the atomic makeup of a specific sample. The method relies on the distinct photophysical signals of individual elements to accurately identify the type and quantity of each element present in a sample. The sample is nebulized and then transferred to an argon plasma. Intense heat decomposes the sample into a cloud of hot gases containing free atoms and ions of the element (s) of interest. The high temperature causes significant collisional excitation and ionization of the sample atoms. Next, they decay to lower states through thermal or radiative (emission) energy transitions. During ICP-OES analysis, the intensity of the light emitted at specific wavelengths is measured and used to determine the concentration of elements of interest after calibration. The standard (calibration) curve is the relationship between instrument response and a known concentration of the analyte. It should cover the entire range of expected concentration. Internal standards are used to adjust variations between samples and differences in how samples are processed (Drava & Minganti, 2020).

2.7. Desulfurization Methods

Desulfurization is a process that efficiently removes sulfur from different types of samples. Various methods have been utilized to remove sulfur compounds. However, sulfur compounds in different forms with numerous properties, including size variance, reactivity, and polarity, make the desulfurization process challenging. Below are some of the methods applied for desulfurization.

2.7.1. Hydrodesulfurization

Hydrodesulfurization is a widely adopted conventional method in refineries to eliminate sulfur compounds in fuels (Cao *et al.*, 2020; X. Liu *et al.*, 2020). It employs hydrogen gas and a catalyst to break down sulfur-containing compounds (C-S bond), forming hydrogen sulfide as a byproduct (Shafi & Hutchings, 2000). The HDS reaction is carried out in trickle-bed reactors, operating at temperatures of 300–400 °C and hydrogen pressures of 20-130 atmospheric pressure with longer residence times (Jantaraksa *et al.*, 2015). Catalysts such as nickel molybdenum/aluminum oxide and cobalt molybdenum/aluminum oxide are commonly applied to eliminate sulfur compounds from liquid fuels effectively (Abro *et al.*, 2014; Jantaraksa *et al.*, 2015; Whitehurst *et al.*, 1998).

Aliphatic sulfur compounds have considerable reactivity and are susceptible to complete removal through hydrodesulfurization (HDS) reactions, as depicted in equations 2.1–2.3 (Javadli & De Klerk, 2012), where R represents an alkyl or other organic substituent,

Thiols: $R\text{-}SH + H_2 \rightarrow R\text{-}H + H_2S$ Equation 2.1
Sulfides: $R_1\text{-}S\text{-}R_2 + 2H_2 \rightarrow R_1\text{-}H + R_2\text{-}H + H_2S$ Equation 2.2
Disulfides: $R_1\text{-}S\text{-}S\text{-}R_2 + 3H_2 \rightarrow R_1\text{-}H + R_2\text{-}H + 2H_2S$ Equation 2.3

According to Babich & Moulijn, (2003a), increasing HDS conditions can improve desulfurization, but elevated temperatures might result in greater coke generation, which leads to catalyst inactivation. Furthermore, higher pressures can cause olefin saturation, ultimately reducing gasoline's octane rating (Babich & Moulijn, 2003a). Yet, the HDS design restricts the intensity of the procedure. Additionally, these intensified conditions have negative consequences, like reduced catalyst lifespan, more hydrogen consumption, and increased yield losses, leading to higher operating costs (Mei *et al.*, 2003).

Generally, if the unpaired electrons of sulfur can resonate with the pi electrons of the organic structure, the energy of the carbon-sulfur bond (C-S) is nearly the same as that of the carbon-carbon (C-C) bond (Smith *et al.*, 1985). Consequently, this diminishes the selectivity of the HDS process and encourages the hydrogenation of carbon-carbon pi-bonds (Attar & Corcoran, 1978). The C-S bond cannot be broken until the aromatic rings are completely saturated, requiring a significant amount of hydrogen. Although the resonance stabilization energy of RS compounds (120–130 kJ mol^{-1}) is relatively lower than that of benzene (160–170 kJ mol^{-1}), it still presents a significant barrier to the efficiency of hydrodesulfurization (HDS) processes, making them energetically demanding for breaking the C–S bond of RS compounds (Javadli & De Klerk, 2012). For instance, 4,6 DMDBT will need either 3 or 4 H_2 molecules to eliminate the sulfur molecule, depending on the mechanism (Babich & Moulijn, 2003a). As a result, sulfur-containing compounds such as dibenzothiophene (DBT) and its alkyl-substituted derivatives pose greater removal challenges due to their hydrogenolysis resistance. The difficulty in removing dialkyl-substituted DBTs is attributed to stearic hindrances arising from the close arrangement of alkyl substituents (Babich & Moulijn, 2003; Kabe *et al.*, 1992; Ma *et al.*, 1994b, 1995; Stanislaus *et al.*, 2010). For instance, Naphthothiophene has high boiling points, leading to its enrichment in high-boiling fractions during direct oil distillation (Ismagilov *et al.*, 2011).

2.7.2. Bio-Desulfurization

Bio-desulfurization utilizes microorganisms that can break down sulfur-containing compounds. It has made remarkable strides in screening specialized strains with high digestibility for sulfur-containing organic matter. This transformative process converts these compounds into water-soluble substances (SO_4^{2-}) through the actions of bacteria or enzymes (Lin *et al.*, 2020). To date, bio-desulfurization has been formed through various paths: the sulfur atom is targeted first in the four-step enzymatic pathway, while the carbon atom is the initial target in the Kodama route (Abro *et al.*, 2014). According to Gupta *et al.* (2005), microorganisms can eliminate sulfur from fossil fuels through three main actions: oxidation C-C cleavage, oxidation C-S cleavage, and reductive C-S cleavage. Based on (Lin *et al.*, 2020), diverse sulfide types and limitations of a single strain can impact the overall effectiveness and application of bio-desulfurization. Addressing the strain lifespan issues is vital for the successful industrial implementation of bio-desulfurization technology. Furthermore, the mass transfer from the oil-water interface to the microbe is slower when compared to the sulfur compound transfer to the interface. This indicates that the metabolism rate is the limiting factor in the process (Guobin *et al.*, 2006). Although it has received considerable attention due to its environmentally friendly processing of fossil fuels, the application of the bio-desulfurization technique is restricted by slow decomposition and biocatalyst compatibility. Additionally, the sensitive nature of living microbes, including factors like pH, temperature, and dissolved oxygen levels, makes their handling in the refinery environment, including storage, shipment, and use, challenging (Campos-Martin *et al.*, 2010).

2.7.3. Extractive Desulfurization using Solvents

Solvent extraction methods are often used in liquid fuels to eliminate sulfur compounds from light oil. The solubility of a substance is a basic characteristic that is used to determine the viability of an extraction process. The solvent used can be recovered and recycled via distillation (Babich & Moulijn, 2003a; Feng, 2010). Nonetheless, sulfur's polarity is slightly different from other aromatic hydrocarbons. Hence, using only solvent extraction leads to a loss of beneficial hydrocarbons and a decreased percentage of removal (Abotsi & Scaroni, 1989; Babich & Moulijn, 2003a; Shiraishi *et al.*, 2002). Therefore, enhancing the polarity of sulfur compounds by employing the oxidation method prior to their removal through extraction has gained interest (Feng, 2010).

2.7.3.1. Solvent Selection Requirements

Solvent extraction is frequently employed in the literature to remove sulfones due to its practicality. The effectiveness of extractive desulfurization depends on the solubility of sulfur compounds in the chosen solvent. Therefore, selecting the right solvent is paramount for successful desulfurization. Various solvents, such as acetone, ethanol, and polyethylene glycols, have undergone testing, yielding desulfurization rates ranging from 50% to 90%, contingent upon the number of extraction cycles employed (Izumi & Tetsuo, 1995; Paulino, 1995). According to E. Guth & A. Diaz, (1974), the choice of solvent is paramount for extracting polar organosulfur compounds, notably sulfones, from biofuel oils. The general requirements for the solvent are as follows.

- It is crucial that the two phases remain immiscible.
- Ability to dissolve oxidized sulfur compounds.
- Relatively low boiling point/ higher volatility for easy separation of solutes (sulfones) and oil.
- Inability to readily form emulsions with the oil.
- Substantial density difference compared to the oil for easy separation.
- Cost-effectiveness compared to oil.
- Ability to maintain the fuel properties of the oil.
- High dielectric constant, which is necessary for estimating the chemical stability and solubility (Sengwa *et al.*, 2009).

2.7.4. Oxidative Desulfurization

Oxidative desulfurization is a method used to remove sulfur compounds from feedstocks via oxidation reactions, with or without a catalyst. During oxidative desulfurization, sulfides are oxidized by adding one or two oxygen atoms to the sulfur with the help of suitable oxidants. This leads to the formation of sulfoxide intermediates, and sulfones when there is an excess oxidant (Attar & Corcoran, 1978; Campos-Martin *et al.*, 2010; Ismagilov *et al.*, 2011). Based on J. Li *et al.* (2020), due to the higher electronegativity of oxygen compared to carbon and sulfur, the sulfur atom in sulfides acts as a nucleophile (a molecule that donates electrons) and attacks the active oxygen atom, forming sulfone compounds. Moreover, Benassi & Taddei (1998) observed that during the oxidation of divalent sulfur species to sulfones, the bond energies of C-S bonds in aliphatic sulfides and aromatic sulfides or thiophenes decreased by 5.2 kcal/mol and 11.8 kcal/mol, respectively. The sulfones have high polarity and can be easily removed (Piscopo *et al.*, 2020). The highly polar sulfones can be efficiently separated through adsorption, extraction, precipitation, or distillation (Kulkarni *et al.*, 2010).

The process of oxidative desulfurization has two key benefits. Firstly, it can be conducted in a liquid phase with mild operating conditions, reducing capital costs. Secondly, it displays strong reactivity and selectivity towards specific sulfide compounds (Feng, 2010). On the contrary, it has two major challenges: 1) the selected oxidants may not exhibit great selectivity, with some leading to undesired side reactions that reduce both the amount and quality of fuel. 2) using unsuitable solvents that can result in the loss of desirable aromatic/olefinic compounds or insufficient sulfur compound extraction (Ali *et al.*, 2006). As a result, choosing the right solvent for extracting sulfur compounds is crucial.

The predominant methods for oxidative desulfurization that have been extensively researched and comprehended utilize H_2O_2 as an oxidant, necessitating a catalyst. Among the commonly utilized acid catalysts are formic acid and acetic acid. Formic acid, while initially considered as an alternative, is not recommended due to the generation of undesirable by-products like sticky polymer materials (Farshi & Shiralizadeh, 2015). Furthermore, it can decompose into carbon monoxide (CO), water (H_2O), and hydrogen gas (H_2) at ambient or elevated temperatures (Ramírez-Verduzco *et al.*, 2004). Therefore, acetic acid was selected as a more suitable alternative for the study. Nevertheless, it is advisable to avoid using these oxidants at high concentrations due to safety concerns and the potential deterioration of oil quality (G. Yu *et al.*, 2005).

In a study conducted by Zannikos *et al.* (1995), they investigated the oxidative desulfurization of straight-run gas oils, primarily containing aliphatic sulfide contaminants. They heated this mixture to 90 °C along with an equal volume of acetic acid and aqueous hydrogen peroxide. After approximately 30 minutes of treatment, they successfully removed up to 90% of the contaminants from the fuels. However, achieving this level of desulfurization required significant quantities of acetic acid and hydrogen peroxide. Additionally, it also necessitated three extractions using polar organic solvents followed by subsequent washings with water. Among the various extractant cosolvents examined, including methanol, N-methyl pyrrolidone, and DMF, methanol exhibited the most effective sulfur removal.

Shiraishi *et al.* (2002) also explored the process of oxidative desulfurization using a combination of H_2O_2 and acetic acid on both model fuels (such as BT, 3-MBT, 2,3-MBT, DBT, 4-MDBT, 4,6-DMDBT, or 2,8-DMDBT in tetradecane) and actual light oils. They established a relationship between the electron densities of the sulfur atom in each contaminant and the corresponding rate constants, noting that higher electron density correlated with increased oxidation rates. Interestingly, they observed a linear relationship within each series, for example, between BT and its derivatives versus DBT and its derivatives. Furthermore, they found that to achieve deep desulfurization levels in the actual oils, an additional extraction step with an organic solvent was necessary due to the slight solubility of the oxidized products in the fuel. They opted for an acetonitrile/water mixture as the preferred solvent for this extraction process.

Ramirez-Verduco and colleagues explored the efficacy of a fundamental oxidative desulfurization system combined with extraction using a polar solvent to eliminate sulfur impurities from real diesel fuel (Ramírez-Verduzco *et al.*, 2004). Employing H_2O_2 (30%) as an oxidizing agent and acetic acid as a catalyst, they achieved a removal rate of 60-62% for stubborn sulfur impurities, varying with the extraction solvent used. This process took 6 hours of stirring at 50°C. In the research conducted by Ahmed *et al.* (2023), the optimal reaction conditions were determined to be a carboxylic acid dosage of 0.6 g and 10 mL of H_2O_2 at a temperature of 95°C. The desulfurization efficiency of the actual diesel sample (2568 mg/L) was demonstrated to be 27%, 34%, and 84.57% after 1 hour using citric acid, α-ketoglutaric acid, and pimelic acid, respectively.

Ozone appears to be an attractive oxidant for the oxidative desulfurization process due to its ease of generation on-site (Oyama, 2000). However, most studies involving ozone as an oxidant for sulfur-containing compounds concentrate on aliphatic substrates rather than the more challenging aromatic species. Moreover, it frequently occurs in aqueous or gaseous environments rather than fuel-like matrices (Fox, 2011). Furthermore, its use requires careful handling due to its reactivity and potential environmental impact. It can also contribute to the formation of ground-level ozone, a harmful air pollutant and component of smog. (Ahmed *et al.*, 2023).

Sampanthar *et al.* (2006) explored oxidative desulfurization by employing air as the oxidant due to its cost-effectiveness, widespread availability, portability, and eco-friendliness. It was done in conjunction with solid-supported manganese and cobalt oxide catalysts. They investigated both model fuels containing various sulfur compounds and actual diesel fuel. Their findings revealed that desulfurization with air and these catalysts was feasible above 110°C, with the ideal temperature range being 130-200°C. After 8 hours at 150°C, approximately 80-90% of sulfur contaminants were removed from model fuels, followed by solvent extraction. Furthermore, they achieved sulfur reduction in actual diesel to levels between 40-60 ppm. However, it was observed that the method decreased the olefin and aromatic content of the fuel, indicating lower selectivity compared to alternative oxidation techniques.

Dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) possess high sulfone extraction capabilities. However, their high boiling points make the separation and reuse processes challenging. Conversely, acetonitrile was selected for its advantageous properties, notably its relatively low boiling point of 82 °C (Campos-Martin *et al.*, 2010). This characteristic allows for easy separation from sulfones through distillation, making it a suitable solvent for extraction purposes (Wan & Yen, 2008).

2.7.4.1. Oxidative Desulfurization Principle/Mechanism

In oxidative desulfurization, the initial stage of the reaction relies on the sulfur atom attacking the hydrogen peroxide. Consequently, the increased electron density due to electron-donating groups will substantially impact the oxidation reaction rate. Furthermore, the location and length of alkyl groups are also expected to influence the electron density of sulfur compounds as previously documented by Shiraishi *et al.* (2002).

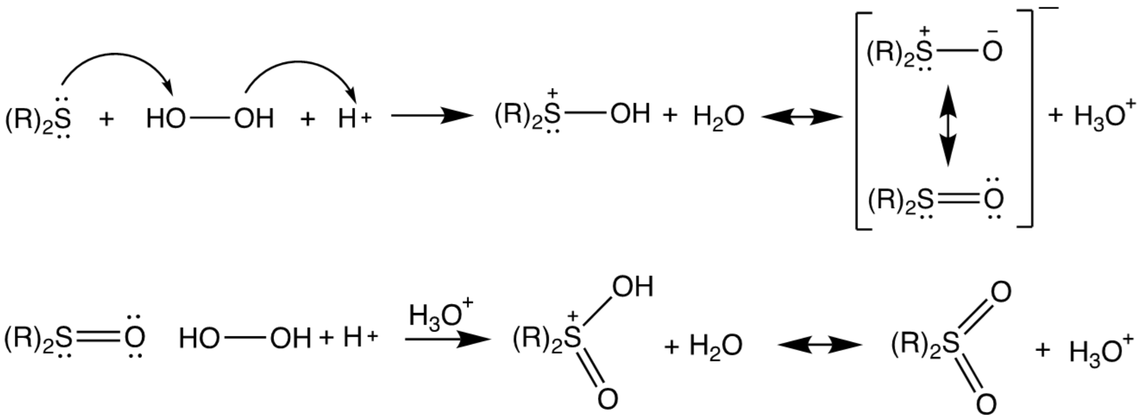


Figure 2.5. Mechanism of hydrogen peroxide attack on sulfur-containing

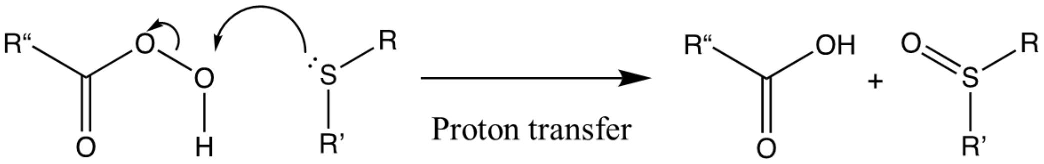


Figure 2.6. Mechanism of sulfur atom attacking terminal peracid oxygen and cleavage of the O-O Bond

(Di Furia & Modena, 1982)

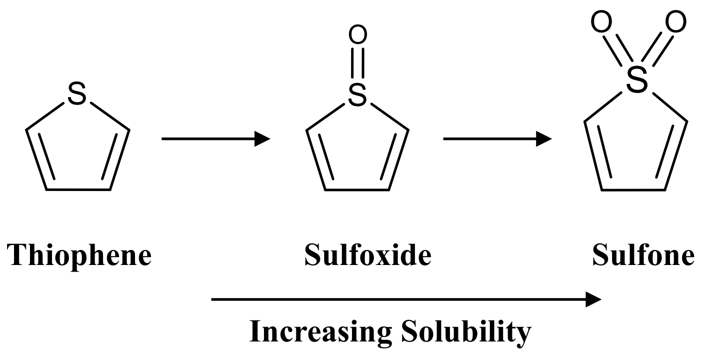


Figure 2.7. Oxidation of Thiophene

2.7.4.2. Ultrasonic Assisted Oxidative Desulfurization

Ultrasonic-assisted oxidative desulfurization is an emerging method that harnesses ultrasonic waves to form a fine emulsion, intensify mixing between immiscible phases, and accelerate the oxidative desulfurization reaction rate (Choi *et al.*, 2014; Khodaei *et al.*, 2017, 2018). Bolla *et al.*, (2012) highlighted the advantageous effects of ultrasonic-assisted oxidative desulfurization, attributing its success to the enhanced interfacial area achieved through fine emulsification of fuel and oxidants. This process creates extreme conditions for oxidation, establishing localized high-temperature and high-pressure environments that concurrently produce free radicals and activated oxygen while reducing solvent usage. Moreover, ultrasonic technology is environmentally friendly (Huang *et al.*, 2018), aligning with the promotion of clean fuel production.

2.7.5. Adsorptive Desulfurization

Adsorptive desulfurization has emerged as an effective clean technology for lowering oxides of sulfur emissions and enhancing fuel oil quality (Zhou *et al.*, 2009). In contrast to the hydrodesulfurization process, adsorptive desulfurization removes sulfur under low temperature and pressure conditions and does not require hydrogen (Dehghan & Anbia, 2017; Zhou *et al.*, 2009). Adsorbents used in adsorptive desulfurization include carbon-based materials (M. Yu *et al.*, 2015), metal adsorbents (such as reduced metals, metal oxides, and metal sulfides) (Sui *et al.*, 2016), silica-based adsorbents (Palomino *et al.*, 2014; Qin *et al.*, 2016), and metal-organic frameworks (Qin *et al.*, 2016).

Carbon-based sorbents, like activated carbons, are advantageous due to their wide availability and low production cost for sulfur compound removal. However, these materials have low thermal and mechanical stability (Nhut *et al.*, 2002). Another category of carbon-based sorbents is ordered mesoporous carbons, which offer biocompatibility, chemical stability in non-oxidizing environments, and mechanical stability. Nevertheless, their hydrophobic and inert properties can pose challenges for use in adsorptive desulfurization applications (Baniamerian *et al.*, 2009). One of the disadvantages of metal adsorbents is their reliance on costly metals or supports in large amounts, and regeneration of these adsorbents for reuse is relatively challenging (Kim *et al.*, 2006). Microporous adsorbents, particularly zeolites, have been extensively studied due to their acidity. However, their exclusive microporous structure limits their effectiveness in removing larger sulfur molecules (Hernández-Maldonado & Yang, 2003; Jeevanandam *et al.*, 2005). To address this limitation, mesoporous materials such as silica were introduced. Nonetheless, the amorphous nature of silica walls and their weak acidity resulted in inadequate performance in sulfur compound adsorption (He *et al.*, 2011; Y. Wang *et al.*, 2008).

Adsorption occurs as the sulfur molecules bind to the adsorbent on the surface and stay isolated from the sample matrix. The effectiveness of adsorbents in adsorption typically relies on a combination of surface chemical characteristics, like the presence and density of active sites, along with physical attributes such as surface area, pore size, and distribution (Kim *et al.*, 2006). A major hurdle in the extraction of sulfur compounds from fuels is finding an adsorbent that can effectively isolate sulfur compounds while avoiding or minimally adsorbing aromatic hydrocarbons and olefins. This difficulty arises from the similarities between thiophene sulfur compounds and pure aromatic and olefinic compounds, including their double bonds, which can interact with metal species (Angelici, 1995; Sánchez-Delgado, 1994). Even though adsorption is very efficient, it can be challenging to regenerate the adsorbents, usually needing calcinations or solvent washing (Hernández-Maldonado & Yang, 2004). Additionally, numerous adsorbents have limited adsorption capacity (Chandra Srivastava, 2012). Economical clay materials can adsorb 1-4 mg of sulfur compound per gram of clay, leading to a need for large quantities of adsorbent. Engineering methods like raising temperature and/or lowering the pressure can disrupt the bonds created through π-complexation, which are stronger than Vander Waals interactions (King & C. J., 1987).

2.7.5.1. Adsorption Types

There are two primary approaches to adsorptive desulfurization:

a) **Physical Adsorption (Physisorption):** In this approach, sulfur compounds are adsorbed onto the surface of a solid sorbent without undergoing any chemical alteration. The adsorption is typically driven by physical forces such as Van der Waals or electrostatic interactions. Since no chemical reactions are involved, the energy required for the sorbent regeneration primarily depends on the strength of adsorption. However, because it is only a physisorption process, the energy demand for regeneration tends to be relatively low.

b) **Reactive/Chemical Adsorption (Chemisorption):** This method involves a chemical reaction between the sulfur compounds and the solid sorbent surface. The sulfur is chemically bound to the sorbent, usually forming sulfide compounds. Regeneration of the sorbent can be achieved through thermal methods, where the sorbent is heated to release the sulfur compounds, or through flushing the spent sorbent with a desorbent material. The desorbent displaces the sulfur compounds from the sorbent surface. Depending on the specific process and feedstock characteristics, sulfur may be removed in the form of hydrogen sulfide (H_2S), sulfur oxides (SO_x), or elemental sulfur (Babich & Moulijn, 2003a).

2.7.5.2. Adsorbents

Adsorbents are natural or synthetic materials with microcrystalline or amorphous structures that feature surface pores, which play a key role in separation processes (Treybal & Kulkarni, 1981). The pore size of these materials is crucial, as it determines the ability of adsorbate species to access and interact with the adsorbent. According to the International Union of Pure and Applied Chemistry, materials with pore diameters smaller than 2 nm are classified as microporous, those with pore sizes between 2 and 50 nm are considered mesoporous, and materials with pores larger than 50 nm are categorized as macroporous (Thommes *et al.*, 2015).

2.7.5.2.1. Bentonite Clay

Clay minerals are a well-known class of natural inorganic materials with well-known structural adsorption and rheological and thermal properties. Clays are hydrous aluminosilicates composed of mixtures of fine-grained clay minerals and clay-sized crystals of other minerals like quartz, carbonate, and metal oxides. The term "clay" applies to materials having a particle size of less than 2 µm (25,400 µm = 1 in.). Additionally, it also applies to the family of minerals having similar chemical compositions and standard crystal structural characteristics (Velde, 1995). The good adsorption ability comes from their negative charge, which can be neutralized by the adsorption of positively charged anions (Mockovčiaková *et al.*, 2009). Common cations and anions found on clay surfaces include Ca^{2+}, Mg^{2+}, H^+, K^+, NH_4^+, Na^+, SO_4^{2-}, Cl^-, PO_4^{3-}, and NO_3^- (Srinivasan, 2011). Both Bronsted and Lewis acidity enhance clay minerals' adsorption capacity significantly. For many years, clay materials have been used for the adsorption of anions such as nitrates (Öztürk & Bektaş, 2004), like phosphates and sulfates, or gas adsorption like CO_2 (Azzouz *et al.*, 2010). The use of clays as adsorbent has advantages over many other commercially available adsorbents in terms of low cost, abundant availability, high specific surface area, excellent adsorption properties, non-toxic nature, and large potential for ion exchange (Crini & Badot, 2011). The application of clay materials is greatly governed by their surface properties like adsorption capacities, surface charges, large surface area, charge density, the type of exchangeable cations, hydroxyl groups on the edges, Lewis and Bronsted acidity (Reddy *et al.*, 2009).

Bentonite is an inorganic 2:1 type clay mineral, which is mainly constituted of montmorillonite (Maged, Iqbal, *et al.*, 2020). This montmorillonite is categorized as a cationic clay mineral (Lingaiah *et al.*, 2005). The structure comprises two silica tetrahedral sheets enclosing an aluminum octahedral sheet (Mockovčiaková *et al.*, 2009). Isomorphous substitution, such as the replacement of trivalent ions like Al^{3+} by divalent ions such as Fe^{2+} or Mg^{2+} in the octahedral layer, or the substitution of Si^{4+} with Al^{3+} in the tetrahedral layer, leads to a net negative electric charge on the clay surface. This negative charge is balanced by Ca^{2+} or Na^+ cations in Na-type or Ca-type bentonite. Accordingly, the clay surface becomes hydrophilic, facilitating expansion when wet, a phenomenon attributed to ion hydration (Shen, 2001). This characteristic limits their effectiveness in adsorbing hydrophobic organic compounds. Consequently, surface modification is necessary to enhance the hydrophobicity of bentonites and improve their interaction with organic compounds

(Yuliana *et al.*, 2020). Due to the excellent sorption and physical and chemical properties of bentonite (i.e., CEC, porosity, particle size, and surface area), bentonite is considered the best candidate for the sorption of different kinds of emerging pollutants (Genç & Dogan, 2015). It has been utilized as an adsorbent for SO_2 (Ersoy-Mericboyu, 1999; Renedo *et al.*, 2006), dimethyl disulfide (Mikhail *et al.*, 2002), dibenzothiophene (Froehner *et al.*, 2010). Furthermore, the ability to modify bentonite by different kinds of modifiers such as organic or inorganic chemicals and acid or alkaline solutions can result in the enhancement of sorption capacity for different kinds of pollutants (Maged, Kharbish, *et al.*, 2020).

2.7.5.2.1.1. Acid Activation and Iron Modification of Bentonite Clay

Surface chemistry and structural modifications can substantially influence the adsorption capacity of adsorbent material. Techniques such as acidification, metal loading, sulfidation, oxidation, and the addition of guest materials are crucial for improving their effectiveness (Ganiyu *et al.*, 2016). An effective adsorbent must offer an active surface, large surface area, and appropriate pore size distribution (Saleh, Sulaiman, AL-Hammadi, *et al.*, 2017). Activation can increase surface area (Altundoan *et al.*, 2002). The acid activation process is pivotal for modifying the physical and chemical properties of bentonites (Rhodes & Brown, 1992). This treatment dissolves impurities like calcite, exposing platelet edges and thereby increasing surface area and pore diameter. Acid activation begins with replacing exchangeable cations with protons (H^+) and partially dissolving tetrahedral and octahedral sheets. This creates new acid sites within the structure, making the particles more porous and enhancing their adsorptive properties (Christidis *et al.*, 1997; Komadel *et al.*, 1990; Srasra *et al.*, 1989; Taylor *et al.*, 1989).

Natural clays are purified and treated with mineral acids. Among these acids, hydrochloric acid and sulfuric acid are the most widely used in acid activation because they give good results regarding the specific surface area, porosity, and adsorption capacity of the activated clay (Valenzuela Díaz & De Souza Santos, 2001). Acid treatment dissolves some Al^{3+}, Fe^{3+}, Mg^{2+} from the lattice structure and causes the exchange of K^+, Na^+, Ca^{2+} by H^+ in the interlamellar spaces (Tyagi *et al.*, 2006). Mikhail *et al.* (2002), explained that when clay undergoes acid treatment, the original cations are replaced with positive hydrogen ions on the clay surface. This process increases the number of acid sites on the surface, which migrate to the clay, disrupting the charge balance within the clay structure. This disruption creates strain, leading to the formation of new active sites for adsorption. Additionally, the acidic nature of the treated clay surface enhances its interaction with more basic compounds. As a result, relatively basic sulfur compounds such as dimethyl disulfide are more readily adsorbed, making acidic clays effective adsorbents. Modifying bentonite clay with Fe (III) will enhance sulfur removal efficiency and adsorption capacity by increasing the surface area and pore size (changing the morphology and microstructure). This is also supported by Ania & Bandosz, (2006), who observed an improved selectivity and capability of adsorbents when adding metals like iron. According to Komadel *et al.* (1990), hydrochloric acid demonstrated greater efficiency compared to sulfuric acid, which in turn surpasses nitric acid in terms of effectiveness.

2.7.5.2.2. Al-MCM-41

Al-MCM-41 is an aluminum-containing mobile composition of matter number 41. It is a mesoporous aluminosilicate material that has been extensively researched due to its distinctive characteristics. This includes a high surface area of 500-1200 m^2/g, large 2-4 nm pores, and a narrow pore size distribution with a pore volume of 1 cm^3/g. Moreover, adding trivalent aluminum atoms into the tetrahedral sites of MCM-41 silica generates low to moderate acidity (Kresge *et al.*, 1992). This acidity plays a great role in the adsorption process. Al-MCM-41 has a uniform mesoporous arrangement in a hexagonal array, aiding in the diffusion of polycyclic sulfur compounds. B. S. Liu *et al.* (2007), suggested using Al-MCM-41 as a desulfurization agent because of its significant pore volume and high specific surface area. Their research showed that introducing aluminum into the mesoporous structure of MCM-41 significantly enhanced sulfur removal from diesel.

3. Materials and Methods

3.1. Materials

Poultry fat (100.0 ± 0.8 ppm) was obtained from West Coast Reduction Ltd. (Calgary, Alberta, Canada), and Brown grease (515 ± 5 ppm) was sourced from Great Lakes Biosystems Inc. (Sturtevant, WI, USA); both were used "as is". Hardwood (1490 ± 40 ppm) and softwood tall oil soap (2040 ± 40 ppm) were procured from a kraft-pulping mill in (Edmonton, Alberta, Canada). The natural bentonite clay was purchased from Sigma Aldrich (Oakville, Ontario, Canada). Amberlyst®-A21 and Amberlite®-IRC50 were sourced from Sigma-Aldrich (St. Louis, MO, USA), while Al-MCM-41 was obtained from ACS Material LLC (Pasadena, USA). These materials were used as received, without modifications except bentonite, as an adsorbent for the desulphurization procedures. Whatman No.4 Qualitative Filter Paper (90 mm diameter) was purchased from GE Healthcare Life Sciences (Amersham, Buckinghamshire, UK) and used for filtration.

Table 3.1. Chemicals and Materials used in the study with supplier information, purity, and location

Name	Purity/ Concentration	Supplier	Location
Acetonitrile (HPLC grade)	>99.9%	Fisher Chemicals	Fair Lawn, New Jersey, USA
Diethylene glycol monomethyl ether (HPLC grade)	>98%		
Hexane (HPLC grade)	>98.5%		
Hydrochloric acid (HCl)	34.37%		
Kerosene (odorless)	-		
Methanol (HPLC grade)	>99.9%		
Toluene	99.8%		

Table (Continued). Chemicals and Materials used in the study with supplier information, purity, and location

Name	Purity/ Concentration	Supplier	Location
Acetic acid (Glacial)	≥99%	Sigma-Aldrich	St. Louis, Missouri, USA
Acetyl chloride	99%		
Chloroform	99.8%		
Diethyl ether	≥99%		
Dioleoyl glycerol	≥99%		
Glyceryl trioleate	≥99%		
Hydrogen peroxide (H_2O_2)	>30%		
Iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$)	>99%		
Nonadecanoic acid methyl ester	99%		
Oleic acid	≥99%		
Phosphomolybdic acid	>99%		
Sodium sulfate (Na_2SO_4)	99%		
Argon (Ar)	99.998%	Linde	Mississauga, Ontario, Canada
Helium (He)	99.998%		
Hydrogen (H_2)	99.998%		
Nitrogen (N_2)	99.998%		
Manganese (Assurance Grade)	1000 µg/mL	Spex®Certiprep	Metuchen, New Jersey, USA
Milli-Q water	-	MilliporeSigma	Burlington, Massachusetts, USA
Nitric acid (HNO_3, Trace metal grade)	67-70%	Fisher Chemicals	Ontario, Canada
Sulfur in hydrocarbon oil	1000 µg/g	PerkinElmer	Manchester, USA
Yttrium in hydrocarbon oil	1000 µg/g	Agilent	Santa Clara, California, USA

Table 3.2. Chemical and physical information on water, acetonitrile, methanol, and diethylene glycol mono ethyl ether

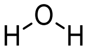
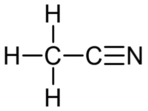
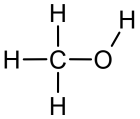
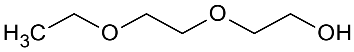
Characteristics	**Water**	**Acetonitrile**	**Methanol**	**Diethylene glycol mono ethyl ether Or 2-(2-Ethoxyethoxy) ethanol**
Chemical formula	H_2O	C_2H_3N	CH_3OH	$C_6H_{14}O_3$
Boiling Point (°C)	100	82	64.7	196
Viscosity (cP)	0.89	0.35	0.54	3.85
Molecular Weight (g/mol)	18.02	41.05	32.04	134.17
Chemical structure		 $\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}C{\equiv}N}$		

Table 3.3. Properties of Adsorbents

Adsorbent	**Functional group**
Bentonite	Hydroxyl and siloxane
Amberlyst®-A21	Tertiary Amine
Amberlite®-IRC50	Carboxylic acid
Al-MCM-41	Silanol

3.2. Methods

3.2.1. Analysis of Total Sulfur Content

The total sulfur content in the sample oils was assessed using the Perkin Elmer Avio 200 inductively coupled plasma–optical emission spectrometry (ICP-OES) instrument (Waltham, Massachusetts, USA). All total sulfur content analyses were conducted at the analytical laboratory within the Department of Agriculture, Food, and Nutritional Science, University of Alberta. Percentage removal of sulfur was computed using the following equation:

$$\%\ \text{Removal} = \frac{(C_i - C_f)}{C_i} \times 100 \qquad \text{Equation 3.1}$$

Where, C_i= initial sulfur concentration C_f= final sulfur concentration

3.2.1.1. ICP-OES Method Development for Sulfur Analysis (Organic Method)

Ensuring precise quantitation is a crucial aspect of method development, and it is essential to validate analytical procedures to achieve accurate results consistently. Therefore, the main target was establishing and validating a precise and reliable ICP-OES method for sulfur detection. For accurate sulfur analysis, utilizing only a sulfur-containing standard solution was crucial. Using a mixture of different element standards resulted in interferences, which compromised the detection of the target analyte. During the evaluation of sulfur content, the wavelength 182.563 nm (radial) exhibited a good response, with high R^2 values of 0.9996. This suggests the method's capability to reliably detect and quantify low concentrations of sulfur in the samples. This outcome aligns with the findings of Froes *et al.* (2007), who also noted that radial arrangements exhibited improved detection capabilities. Low values of the Limit of Quantification (LOQ) and Limit of Detection (LOD) would be preferable for sensitive and accurate analysis. To determine the LOD and LOQ, this study multiplied the relative standard deviation (RSD) of the blank by 3.3 and 10, respectively, and divided by the calibration curve's slope. These calculations establish the minimum sensitivity needed to detect and measure the sulfur present in the samples. As a result, at 182.563 nm (radial), the LOD and LOQ were found to be 0.1 and 0.2, respectively. Based on Gao & Zhang, (2015), the wavelength of yttrium typically does not coincide with that of other elements in the sample. Additionally, compared to other internal standards, such as cobalt and scandium, yttrium had the least amount of sulfur. As a result, this study used it as an internal standard at a final concentration of 1 ppm to prevent undesired interferences. Lastly, the samples were diluted in kerosene. Calibration data directly compared the sample's light intensity and known sample concentration. This analysis gave details about the elements in the sample, which are the main results obtained from ICP-OES. Three readings were taken at a wavelength of 182.563 nm in radial reading for sulfur and at 371.029 nm in radial reading for yttrium. The returning average values were corrected by the recovery of the internal standard and the relative standard deviation of the readings. Sample flow was set at 1 mL/min, with a flush time of 20 seconds. Plasma flow was set at 15 L/min of argon at 1500 W, with the auxiliary gas at 0.8 L/min and the nebulizer at 0.5 L/min. The purge gas (nitrogen) was set at high to reduce the amount of oxygen in the plasma chamber.

3.2.2. Feedstock Characterization

3.2.2.1. Moisture Content

The moisture content analysis in the samples adhered to ISO 662:2016(E) standards for animal and vegetable fats and oils. Initially, crucibles were cleaned, washed, and dried at 103 ± 2 °C in an oven (Isotemp oven, Fisher Scientific, (Waltham, Massachusetts, USA)) for 1 h. After attaining consistent weight through successive weighing, 5 g of the sample oils were deposited into a pre-weighed crucible (nearest 0.001 g). Subsequently, the crucibles containing the oil samples were dried at 103 ± 2 °C for 1 h. Post-drying, they were allowed to cool to room temperature in a desiccator before undergoing the final weighing.

The moisture and volatile matter content, w, expressed as a percentage by mass, is equal to:

$$w = \frac{(m_1 - m_2)}{(m_1 - m_0)} \times 100\% \qquad \text{Equation 3.2}$$

Where, m_0 is the mass, in grams, of the empty crucible.

m_1 is the mass, in grams, of the crucible and sample oil before heating.

m_2 is the mass, in grams, of the crucible and residue after heating.

3.2.2.2. Ash Content

Samples were tested for ash content following the standards outlined in ISO 6884:2008(E) for animal and vegetable fats and oils. Initially, crucibles were washed and dried in a muffle furnace (48000 Furnace, Barnstead (Dubuque, Iowa, USA)) at 500 °C for 2 h to ensure cleanliness and eliminate residual moisture. Once dried, the crucibles were weighed until consistent weight was achieved to affirm precise measurements. Subsequently, 5 g of the sample oils were placed in a pre-weighed crucible. The crucibles, containing the oil samples, were then subjected to an ashing process at 550 °C in the muffle furnace for a duration of 4 h. After the ashing process, the crucibles, along with the oil samples, were left to cool overnight within the muffle furnace and subsequently transferred to a desiccator to achieve stabilization. Then, when a stable weight is reached, record the crucibles with the oil samples after the ashing process.

The ash yield, W, expressed as a percentage mass fraction, is given by the equation:

$$W = \frac{(m_2 - m_1)}{m_0} \times 100 \qquad \text{Equation 3.3}$$

Where, m_0 is the mass, in grams, of sample oil on the dry basis.

m_1 is the mass, in grams, of the empty crucible.

m_2 is the mass, in grams, of the crucible and ash.

3.2.3. Crude Tall Oil Extraction from Tall Oil Soap

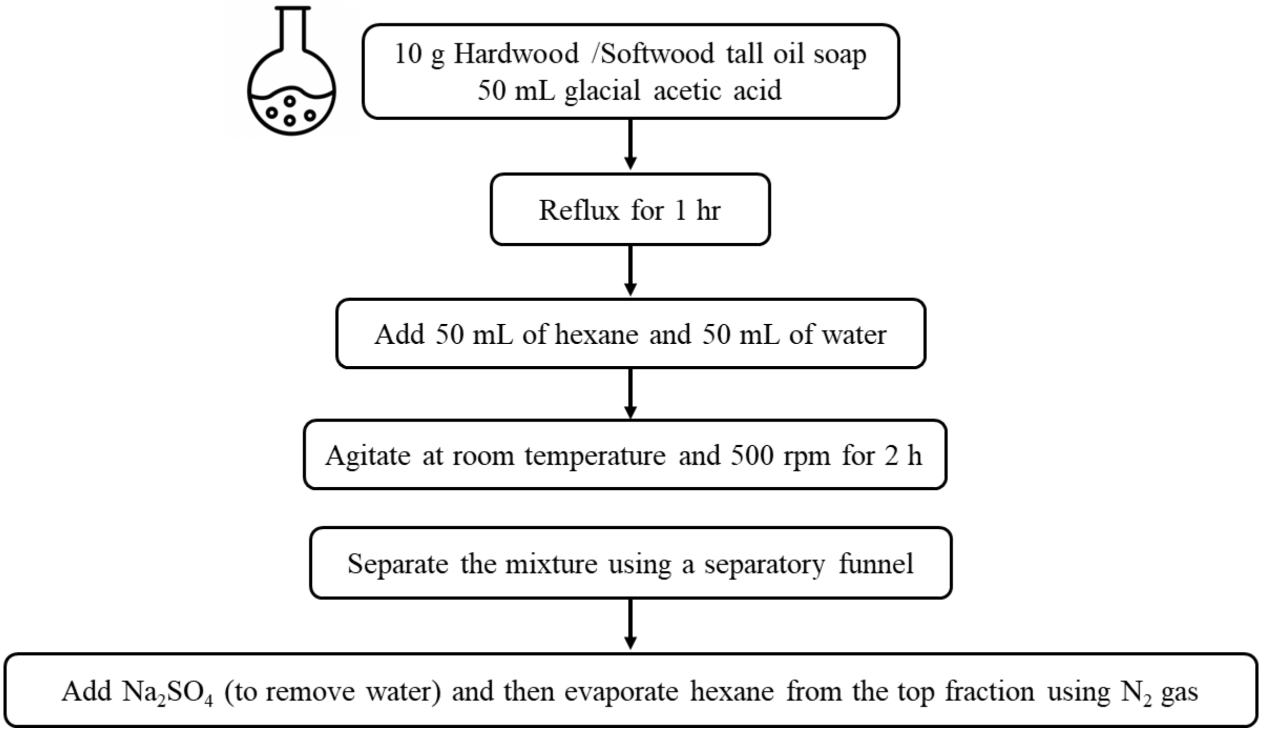


Figure 3.1. Process flow diagram of crude tall oil extraction from hardwood/softwood tall oil soap

Method adapted and modified from Evdokimov *et al.*, (2014)

3.2.4. Characterization of Extracted Fatty Acids

3.2.4.1. Thin Layer Chromatography

The lipid classes of extracted crude tall oils were analyzed using Thin Layer Chromatography (TLC) on a Whatman TLC silica gel plate with a 250 µm layer and polyester backing (Maidstone, Kent, UK). Reference compounds, including glyceryl trioleate (≥99%), dioleoyl glycerol (≥99%), and oleic acid (≥99%) were dissolved in chloroform at a concentration of 5 mg/mL to be used as standards. The mobile phase consisted of a combination of hexane, diethyl ether, and acetic acid at a volumetric ratio of 80:20:1. This method facilitated the differentiation of diacylglyceride, triacylglyceride, and free fatty acids based on their polarity. Chromatographic plates were stained using phosphomolybdic acid in 10% ethanol to visualize and identify components in the analyzed samples.

3.2.4.2. Fourier Transform Infrared Spectroscopy – Attenuated Total Reflectance (FTIR–ATR)

Pure oleic acid, tall oil soaps, and extracted crude tall oils were analyzed by Fourier Transform Infrared Spectroscopy equipped with Universal Attenuated Total Reflectance (Frontier Perkin Elmer (Waltham, Massachusetts, USA)). This aids in obtaining spectral information. A sampling accessory with a Zn-Se diamond prism was used. FTIR-ATR was carried out at room temperature using a resolution of 4cm^{-1} and eight running scans to analyze the presence or absence of the functional groups of the samples in the range of 4000-650 cm^{-1}. This instrument was also used to characterize raw and modified bentonite adsorbents under the same conditions. The samples were pressed with a high-pressure clamp to ensure good contact between the sample and the diamond crystal.

3.2.4.3. Gas Chromatography-Mass Spectrometry-Flame Ionization Detector

The identification of free fatty acid contents and other resin acid compounds was investigated through GC coupled with mass spectrometry. It was quantified via GC with a flame ionization detector. GC-MS analysis was conducted using an Agilent 5975B EI/CI MS instrument in electron ionization (EI) mode. An Agilent 6890N GC-FID equipped with an Agilent HP 7683 autosampler was used for the analysis. The derivatization process involved treating 50 mg of extracted fatty acids from softwood and hardwood tall oil with 1.5 mL of acetyl chloride in 10% methanol. Nonadecanoic acid was used as an internal standard. The mixture was heated at 80 °C for 1 hour in a water bath. This method was described by Lepage & Roy, (1984). Subsequently, 1.5 mL of water and 3 mL of hexane were added in a 1:1 volumetric ratio (polar: non-polar) to the mixture after cooling them to room temperature. This process converted fatty acids into their methyl ester derivatives, improving resolution for GC analysis. An Agilent 6890N GC-FID equipped with an Agilent HP 7683 auto sampler was used for the analysis. A 100 m × 0.25 mm DB-Petro capillary column with a 0.5 µm film thickness was employed. The injector and detector were maintained at constant temperatures of 300 °C and 350 °C, respectively. The GC oven temperature program was initiated at 35 °C for 0.1 min and increased at a rate of 10 °C per minute to reach 280 °C. This temperature was maintained for an additional 15.4 min, resulting in a total run time of 40 min. Helium served as the carrier gas at a consistent flow rate of 1.7 mL/min, with a 1:30 split injection of 1 µL volume. Additionally, GC-MS analysis was performed using an Agilent 5975B EI/CI MS instrument in electron ionization (EI) mode, in combination with the Agilent GC 6890N. The GC-

MS interface temperature was maintained at 320 °C, with a scan range of 10-550 *m/z*, source temperature at 250 ˚C, and Quad temperature at 150 ˚C. The GC setup and conditions were similar to those of the GC-FID for comprehensive compound analysis.

3.2.5. Extractive Desulfurization using Solvents

3.2.5.1. Poultry Fat and Brown Grease

During extractive desulfurization, 75 mL of water, acetonitrile, methanol, and diethylene glycol mono ethyl ether were individually mixed with 15 grams of poultry fat/brown grease in four different flasks, at a 20% feed-to-solvent (w/v) ratio. The mixtures were washed for 2 hours at a speed of 750 rpm, followed by a 30-minute wash with 30 mL of water. This is to remove any remaining solvents from the organic phase. Next, the mixtures were centrifuged at 5000 rpm for 5 minutes (Centrifuge accuSpin 400, Fisher Scientific, (Waltham, Massachusetts, USA)). After that, the organic phases were separated from the aqueous phase. Lastly, the organic fractions were diluted with kerosene, and the resulting solutions were analyzed using ICP-OES to determine the sulfur content.

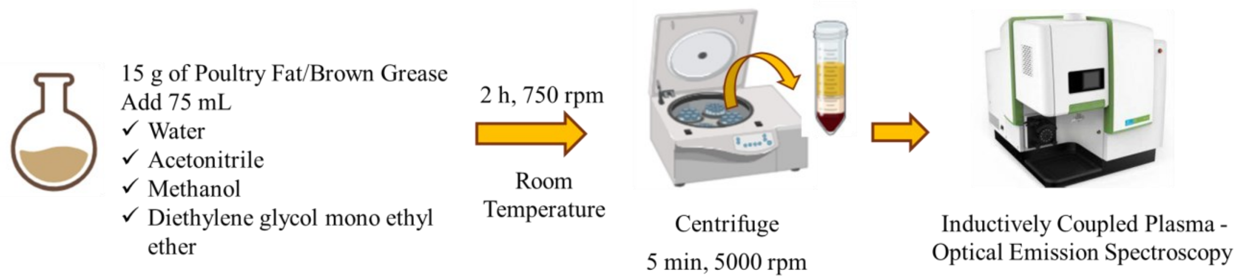


Figure 3.2. Graphical representation of extractive desulfurization of poultry fat/brown grease using solvents

3.2.5.2. Tall Oil Soap

As tall oil soap was a complex composition of resin acids, salts, and fatty acids, measuring the initial sulfur content using the same method as for poultry fat and brown grease was challenging. This was due to its incomplete solubility in solvents. Therefore, the previous method in section 3.2.5.1 had to be modified to analyze the sulfur content of fatty acids, which are crucial components in biofuel production. Hence, the sulfur content of the crude tall oils extracted from tall oil soap and treated with water was used as a baseline to determine the percentage removal of sulfur when treated with other solvents such as acetonitrile, methanol, and diethylene glycol mono ethyl ether.

Initially, four round bottom flasks were prepared, each containing 10 g of hardwood/softwood tall oil soap and 50 mL of glacial acetic acid (in a 1:5 m/v ratio). Then, the mixture was refluxed for 1 hour and was allowed to cool down to room temperature. Subsequently, 50 mL of water, acetonitrile, methanol, and diethylene glycol mono ethyl ether solvents were added to the prepared flasks. Afterward, 50 mL of hexane was added to each flask in a 1:1 volumetric ratio to facilitate the extraction of fatty acids from the composition of tall oil soap. Then, the resulting mixture was agitated for 2 hours at 500 rpm. Following that, the hexane fraction containing the fatty acids were separated using a separatory funnel and filtered using folded Whatman filter paper and a glass funnel. In the end, hexane was evaporated using nitrogen gas.

3.2.6. Oxidative Desulfurization

3.2.6.1. Exploring Effects of Varied Operating Conditions on Percentage Sulfur Removal during Oxidation

Oxidative desulfurization is affected by different factors. To identify the optimal conditions for maximum sulfur removal, the study examined how various operating conditions impact the percentage of sulfur removal. Specifically, it investigated the effects of temperature, catalyst-oxidant molar ratio, and catalyst-oxidant concentration relative to feedstock on the oxidation of sulfur compounds.

3.2.6.2. Effect of Temperature

Fifteen grams of poultry fat/brown grease were mixed with acetic acid and hydrogen peroxide at a molar ratio of 1:3.57 and 36.5% w/w catalyst-oxidant over feedstock concentration. The mixture underwent heating at 60 °C and 90 °C for 1.5 h with continuous stirring at 750 rpm. Subsequently, 75 mL of water (20% w/v ratio of feed to solvent) was added, followed by a 2 h washing process at 750 rpm. Then, a second wash was conducted with 30 mL of water for 30 minutes. This was intended to remove any remaining solvents from the organic phase when using solvents other than water in the upcoming experiments, ensuring equal comparison under the same washing periods. The mixture was centrifuged at 5000 rpm for 5 minutes. After that, the organic phase was separated from the aqueous phase. Lastly, the organic fraction was diluted with kerosene, and the resulting solution was analyzed using ICP-OES for sulfur determination.

3.2.6.3. Effect of Catalyst-Oxidant Molar Ratio

Fifteen grams of poultry fat/brown grease were mixed with acetic acid and hydrogen peroxide at molar ratios of 1:0.89 and 1:3.57. The mixture underwent heating at 90 °C (based on the result obtained from section 3.2.6.2) for 1.5 h with continuous stirring at 750 rpm. The subsequent washing and analysis steps were conducted in the same manner as described in section 3.2.6.2, ensuring consistency across experiments.

3.2.6.4. Effect of Catalyst-Oxidant Concentration Relative to Feedstock

Fifteen grams of poultry fat/brown grease were mixed with acetic acid and hydrogen peroxide at a consistent molar ratio of 1:3.57 but different catalyst-oxidant over feedstock concentrations of 36.5% and 73% w/w. Similarly, another set involved a molar ratio of 1:0.89 but a different catalyst-oxidant over feedstock concentration of 25.74% and 51.48% w/w. The mixture underwent heating at 90 °C (based on the result obtained from the previous section 3.2.6.2) for 1.5 h with continuous stirring at 750 rpm. The subsequent washing and analysis steps were conducted in the same manner as described in section 3.2.6.2, ensuring consistency across experiments.

3.2.6.5. Experimental Procedure for Oxidative Desulfurization

The oxidative desulfurization process was carried out in a batch process with two different experimental setups: one with a temperature-controlled magnetic stirrer hot plate at 750 rpm and another using an ultrasonicator (Crest Ultrasonics (Malaysia), Cortland, New York, USA). The mixture was heated at 90 °C for 1.5 hours in both arrangements. In each experiment, fifteen grams of poultry fat/brown grease was mixed with acetic acid and hydrogen peroxide at a molar ratio of 1:3.57 and 36.5% w/w of catalyst-oxidant concentration relative to feedstock. This was based on the results obtained from the previous sections (3.2.6.3 and 3.2.6.4). Afterward, the resulting mixture was cooled to room temperature. Then, the subsequent washing and analysis steps were conducted in the same manner as described in section 3.2.6.2, ensuring consistency across experiments. Meticulous operations are crucial to mitigate potential hazards.

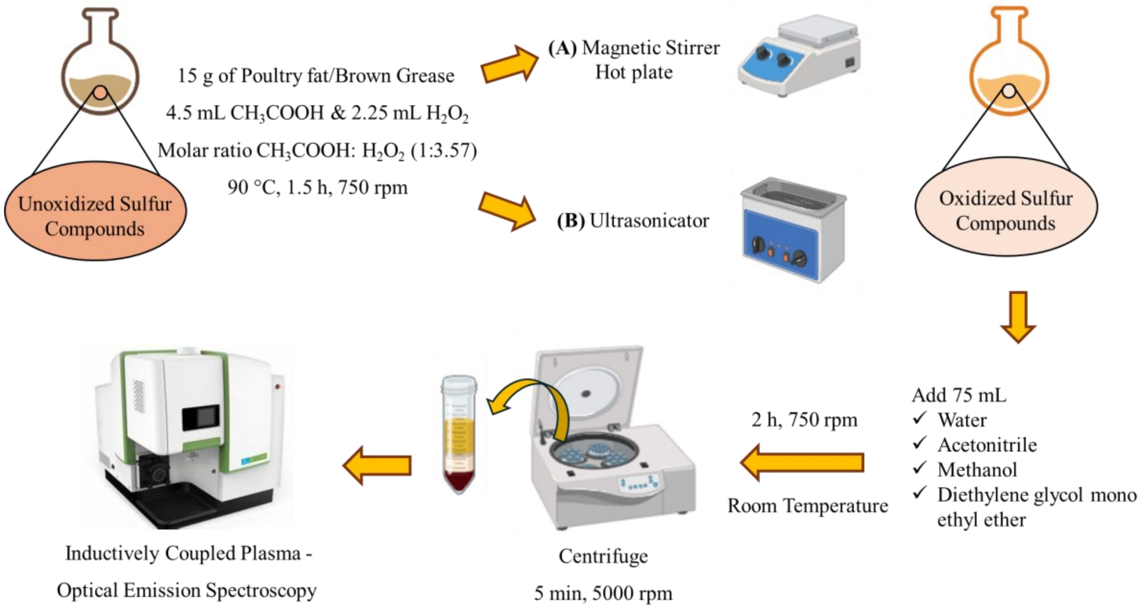


Figure 3.3. Graphical representation of oxidative desulfurization of poultry fat/brown grease using Acetic Acid and H_2O_2

3.2.7. Adsorptive Desulfurization

3.2.7.1. Acid Activation and Modification of Bentonite Clay Adsorbent

The acid activation process was conducted with the aim of enhancing the specific surface area of bentonite. In this procedure, 5 grams of raw bentonite was mixed with 100 mL of 0.1 M HCl in an adsorbent-to-acid solution ratio of 1 g to 20 mL (m/v). After that, the resulting mixture was stirred continuously for 1 hour at 500 rpm. Next, the treated bentonites were filtered out from the solution using a vacuum filter and were thoroughly washed multiple times with milli-Q water until reaching a near pH of 7. Following that, the activated bentonite was dried in an oven at 110 °C for 8 h (Isotemp oven, Fisher Scientific, (Waltham, Massachusetts, USA)). Then, it was powdered with a mortar and pestle and sieved to pass 150 µm mesh screen. Lastly, these samples were stored in a tightly closed container until further use. The method was adapted from Al-Bidry & Azeez (2020). The acid-activated bentonite was then mixed with a 0.08 M $FeCl_3.6H_2O$ solution in a ratio of 1 g adsorbent to 10 mL iron solution (m/v). Next, the combination was stirred at 500 rpm for one hour at room temperature. Then, the mixture was vacuum-filtered and oven-dried at 110 °C for 8 h. Lastly, the dried adsorbent was powdered with a mortar and pestle and sieved through a 150 µm mesh for future use.

3.2.7.2. Experimental Procedure for Ultrasonic-Assisted Adsorptive Desulfurization

5 mL of poultry fat/brown grease was mixed with 0.6 g of adsorbents, including Raw Bentonite, 0.1 M HCl treated Bentonite, 0.08 M Iron impregnated Bentonite, Amberlyst®-A21, Amberlite®-IRC50, and Al-MCM-41. After being ultrasonicated for 5 hours at 40 °C, the mixture was centrifuged at 5000 rpm for 5 minutes to separate the samples from the adsorbents. Lastly, the organic fractions were diluted with kerosene, and the resulting solutions were analyzed using ICP-OES to determine the sulfur content.

The iron impregnation was assessed by quantifying the starting iron concentration in 0.08 M $FeCl_3.6H_2O$ in parts per million (ppm) using ICP-OES. Then, the filtrate post-adsorption process was measured for raw bentonite and bentonite washed with 0.1 M HCl. The goal was to confirm the amount of iron adsorbed on the bentonite clay. The amount of iron impregnated into the bentonite clay was determined using the following equation:

$$\%\text{ iron impregnated} = 100 - \left(\frac{(C_i - C_f)}{C_i} \times 100\right) \qquad \text{Equation 3.4}$$

Where, C_i= initial iron concentration (ppm) C_f= final iron concentration (ppm)

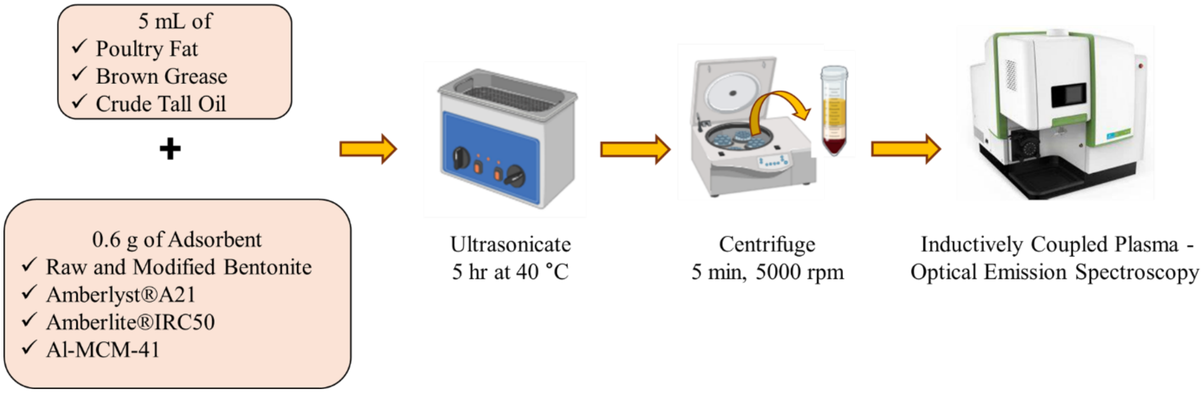


Figure 3.4. Graphical representation of ultrasonic-assisted adsorptive desulfurization of feeds using adsorbents

3.2.8. Desulfurization during the Thermochemical Conversion of Non-Edible Lipids into Diesel-Equivalents

Exploring the desulfurization process during the thermochemical conversion of non-edible lipids into diesel equivalents involved hydrolysis, pyrolysis, caustic washing, and distillation processes. This study processed poultry fat and brown grease into diesel equivalents and conducted subsequent percentage sulfur removal analysis. In this context, diesel equivalent denotes a hydrocarbon within the diesel boiling range that has fuel characteristics comparable to those of traditional petroleum diesel.

3.2.9. Processes Involved in Diesel-Equivalent Production

3.2.9.1. Hydrolysis Process

The hydrolysis of poultry fat and brown grease was conducted in a 5.5 L batch stainless steel reactor (Parr Series 4580, Parr Instrument Company, Moline, IL, USA). The temperature was 280 °C, and the initial pressure was 500 psi. The reaction pressure reached up to 1400 – 1450 psi within 2 h, with an agitation speed of 200 rpm. These parameters were used based on previous studies, which resulted in high conversion rates (Asomaning *et al.*, 2014b). The reaction time was started when the set temperature was reached, and the heater was turned off at the end of the reaction. The reactor was cooled to room temperature by an external cooling system (VWR, Radnor, PA, USA) set to -20 °C. Following that, the hydrolysis products were separated using a separatory funnel. The mass ratio of the sample oil to water was maintained at 1:1 (g/g), with specific quantities for each sample type. For every 1 mol of sample oil, 49 mols of water were used to promote the hydrolysis of triacylglycerols into free fatty acids. Hydrolysis is a reversible reaction, so a second hydrolysis was conducted to ensure maximum conversion. In the first hydrolysis, glycerol was removed, and freshwater was added for the second hydrolysis to convert any remaining triacylglycerols. This systematic approach ensured the efficient conversion of fat into free fatty acids for further processing into diesel fuel.

3.2.9.1.1. Determining Acyl Glycerol Composition Using High-Performance Liquid Chromatography

Acylglycerol composition was determined using HPLC. The triacylglycerols (TAGs), diacylglycerols (DAGs), monoacylglycerols (MAGs), and free fatty acids (FFAs) in poultry fat and brown grease were analyzed. An Agilent LC 1200 HPLC system equipped with evaporative light scattering detector (Agilent Technologies, Santa Clara, CA, USA) was employed for the analysis. The method also utilized a Phenogel column (300mm x 7.8mm ID x 5μm) (Phenomenex, Terrence, CA, USA). The procedure followed was based on the method described by Kittirattanapiboon *et al.* (2008), using toluene containing acetic acid at a concentration of 0.25%.

3.2.9.2. Pyrolysis Process

Pyrolysis reactions were conducted in a stirred 1 L tank reactor (Parr Instrument Co., Moline IL, USA) heated by an electric heating element located outside of the reactor vessel. Thermocouples enabled the real-time measurements of the reactor's internal temperature, and pressure transducers allowed the measurement of the reactor's internal pressure. Each reaction was conducted by initially loading approximately 175 g of fatty acid from the hydrolysis reaction into the reactor vessel. The reactor was checked for leaks and purged with nitrogen at 500 psi. The heater and stirrer at 200 rpm were then turned on. Reactions were carried out at 410 °C and 150 psi after the set temperature was reached for a duration of 8 to 10 hours. The pyrolysis conditions were selected based on initial work conducted by Asomaning *et al.* (2014b). This was to maximize conversion and liquid product yields while at the same time minimizing gas, aromatic, and solid formation. The reactor pressure increased throughout the reaction. The feed input flow rate was set at 3 mL/min, while the product output flow rate averaged at 2 mL/min. Gas and liquid products were collected every hour during the process, enabling real-time pyrolysis process monitoring. This method facilitated timely adjustments, ensured process control, and maintained high product quality. At the end of the reaction, the heater was stopped, and the heating mantle was removed from the reactor vessel to cool.

3.2.9.3. Caustic Washing

Caustic washing of the pyrolyzed products was carried out using a 3 M NaOH solution. The pyrolyzed product was mixed with 300 mL of NaOH solution in a 1:1 (v/v) ratio. The washing process was repeated three times, followed by a fourth wash with water. This process helped remove unconverted free fatty acids, as they could react with Na and form soap, thus enhancing the purity of the resulting diesel-like products. Fourier Transform Infrared (FTIR) analysis was employed to assess the presence of free fatty acids in the samples.

3.2.9.4. Distillation

The distillation process aimed to separate the components based on their boiling points, isolating the diesel fraction from other byproducts generated during the pyrolysis process. The pyrolyzed liquid samples were distilled at atmospheric pressure using a spinning band distillation unit (B/R Instrument M690) with a Teflon band length of 90 cm. The spinning speed was set at 5000 rpm based on the manufacturer's recommendation for the Teflon spinning band. The pyrolyzed sample was transferred to a pre-weighed round bottom flask, and the sample's mass was recorded. Heating was set at 1 °C/min before boiling up and 0.5 °C/min afterward. The heating rate and power percent of the heating mantle were controlled using a temperature controller (J-KEM Scientific Temperature Controller, Model 210). The coolant temperature was also controlled and adjusted at -10°C during the distillation run. The system was allowed to equilibrate for 5 minutes, then the collection was opened when the vapor temperature reached 25°C, with a reflux ratio of 2:1. After that, the temperature of the boiling flask and the vapor temperature were recorded. The distillate obtained at specific vapor temperature ranges was collected as a fraction in a pre-weighed receiver. Then, its volume and mass were recorded. The process was stopped when the vapor temperature reached 160.0 °C. The remaining sample in the flask (bottoms), with a vapor temperature above 160.0 °C was termed diesel equivalent. This fraction was then collected and analyzed for sulfur content.

4. Result and Discussion

4.1. Moisture Content

Moisture content was determined by measuring the weight of the sample before and after removing water and volatile substances. Table 4.1 provides moisture content values for poultry fat, brown grease, hardwood tall oil soap, and softwood tall oil soap. Poultry fat had a very low moisture content, possibly due to the presence of hydrophobic triacylglycerols that have minimal interaction with water. Any water present could have been eliminated during the rendering and refining processes. The observed moisture content of brown grease could be attributed to its heterogeneous nature, which may include water, free fatty acids, and impurities such as food particles and cleaning agents. These impurities could have trapped water molecules, leading to higher moisture content than poultry fat. According to Spiller *et al.* (2020), brown grease contains high moisture and free fatty acids. The high moisture content of hardwood and softwood tall oil soaps might be due to the hydrophilic nature of these soap molecules, particularly the carboxylate anions (R-COO^-), which could readily attract and bind water molecules through hydrogen bonding. The percentage difference might be attributed to the variation in the composition of fatty acids and resin acids between hardwood and softwood sources. Williams *et al.* (2017) states that high moisture content can adversely affect feedstock storage, supply, and transportation to biorefineries. Furthermore, microbial growth, degradation, and spoilage compromise feedstock quality and availability. Lastly, excessive moisture content can increase feedstock weight and volume, resulting in higher transportation costs and logistical challenges. With its low moisture content, poultry fat would be more stable and less prone to such issues. Hence, determining the moisture content was crucial.

Table 4.1. Moisture content of samples (Based on ISO 662:2016(E))

Sample Name	Moisture Content (%)
Poultry fat	0.060 ± 0.001
Brown grease	2.8 ± 0.1
Hardwood tall oil soap	17 ± 1
Softwood tall oil soap	15 ± 1

Values are expressed as mean ± standard deviation (n = 3)

4.2. Ash Content

Ash content was determined from the loss of weight, which occurred during the complete oxidation of the sample at high temperatures through the volatilization of organic materials. Table 4.2 shows the percentage ash content of poultry fat, brown grease, hardwood, and softwood tall oil soap. The variation observed between the samples displayed their diverse composition and origin. Poultry fat had the lowest ash content, possibly due to the relatively pure nature of rendered fat, which primarily consists of triacylglycerols with trace amounts of inorganic impurities. Whereas brown grease had a slightly higher ash content than poultry fat. Being collected from waste cooking oils and fats, the impurities of brown grease could be minerals and metals originating from food particles, cleaning agents, and other residual processing aids. On the other hand, tall oil soaps from hardwood and softwood had the highest ash content, indicating the presence of inorganic, non-combustible impurities. These impurities could be sodium or potassium salts, which may have come from the pulping process.

Table 4.2. Ash content of samples (Based on ISO 6884:2008(E))

Sample Name	Ash Content (%)
Poultry fat	0.132 ± 0.005
Brown grease	0.20 ± 0.01
Hardwood tall oil soap	13.0 ± 0.2
Softwood tall oil soap	15.22 ± 0.03

Values are expressed as mean ± standard deviation (n = 3).

4.3. Analysis of Crude Tall Oil Extraction from Tall Oil Soap

Tall oil soap can be transformed into crude tall oil (CTO) through acidulation. This involved substituting the sodium salt component of the soap with hydrogen ions, forming carboxylic acid from the released resin and fatty constituents (Mag *et al.*, 1983). The effectiveness of extracting crude tall oils from tall oil soaps using glacial acetic acid, hexane, and water is provided in Table 4.3. At the same time, the percentage of non-extractable substances was provided as the insoluble dry mass of impurities. These non-extractable substances could be lignin and/or fiber (S. Y. Lee *et al.*, 2006). The experiment proved that tall oil soaps of hardwood and softwood contained substantial amounts of extractable substances and insoluble impurities. The results indicated that half of the soap's content dissolved in hexane after being treated with acetic acid. The hardwood type displayed slightly greater extraction effectiveness and impurity content, possibly due to differences in the varieties and quantities of fatty acids, resin acids, plant species, and other constituents.

Table 4.3. Extraction efficiency of crude tall oil and dry mass of insoluble impurities in hardwood and softwood tall oil soaps

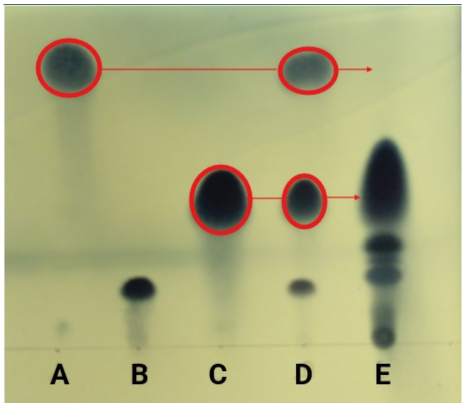
Sample Name	Extraction Efficiency (%)	Dry Mass of Insoluble Impurities (%)
Hardwood tall oil soap	53.2 ± 0.3	10.7 ± 0.8
Softwood tall oil soap	49.5 ± 0.8	7.7 ± 0.2

Values are expressed as mean ± standard deviation (n = 3).

4.4. Characterization of Extracted Crude Tall Oils

4.4.1. Thin-Layer Chromatographic Analysis

Thin-layer chromatography was employed to observe the acylglycerol composition of extracted crude tall oils (Figure 4.1). The results indicated the absence of triacylglycerol and highlighted the predominance of free fatty acids as the main component. The analysis also proved the presence of diacylglycerol.



A: Triacylglycerol
B: Diacylglycerol
C: Free fatty acids
D: Mixture
E: Extracted crude tall oil

Figure 4.1. Thin-layer chromatography (silica plate) of extracted crude tall oils. A mobile phase of hexane, diethyl ether, and acetic acid (80:20:1) was used.

4.4.2. Fourier-Transform Infrared Spectroscopy (FT-IR) Analysis

FTIR-ATR analysis was conducted for pure oleic acids, tall oil soaps, and extracted crude tall oils to get spectral information (Figure 4.2). The analysis revealed specific functional group vibrations, with oleic acid showing strong peaks at 2923 cm^{-1}, 2854 cm^{-1}, and 1708 cm^{-1}, corresponding to the C-H of methyl and methylene groups and the carbonyl bonds (C=O stretching) of carboxylic acids (Koca *et al.*, 2007). The carboxylic group stretching was not observed in the case of hardwood and softwood tall soaps. However, after extracting hardwood and softwood crude tall oils, a distinct stretching pattern characteristic of the carboxylic group peak was observed at 1708 cm^{-1} and 1705 cm^{-1}, respectively. This confirmed the transformation of soap into free fatty acids. The slight differences in peak intensities could potentially be due to differences in fatty acid composition or the presence of impurities. Additionally, the presence of water in hardwood and softwood tall oil soaps was detected through the OH stretching, which appeared at 3420 cm^{-1} and 3392 cm^{-1}, respectively. This aligns with the high moisture content findings from the previous analysis. Bands for short-chain fatty acids were seen in the finger-print region at 1412 cm^{-1} and 1243 cm^{-1}, representing C-O-H in-plane bending and C-O stretching out-of-plane bending, respectively (Koca *et al.*, 2007). Overall, the FTIR analysis confirmed the successful extraction of crude tall oil from tall oil soap.

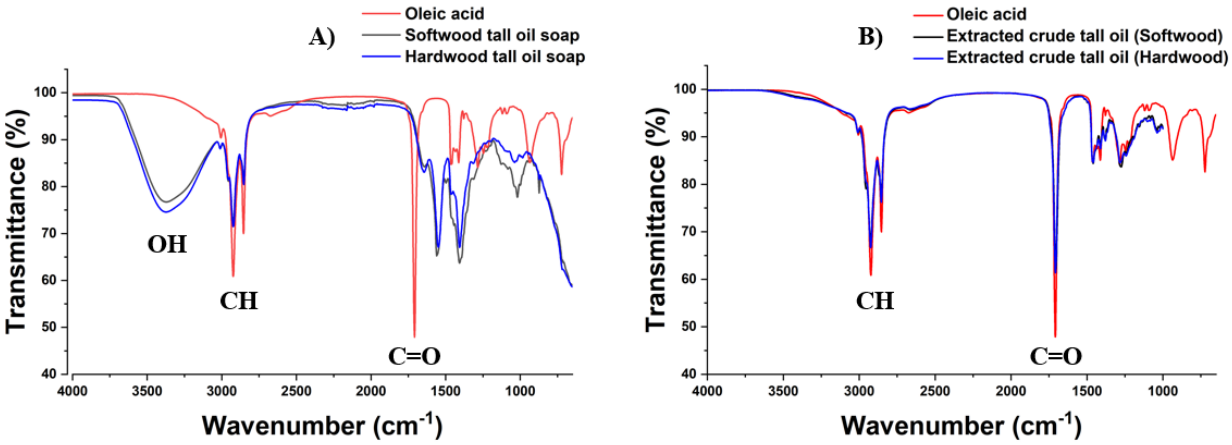


Figure 4.2. FTIR analysis of tall oil soap compared to pure oleic acid **A)** Before extraction of crude tall oil and **B)** After extraction of crude tall oil

4.4.3. Gas Chromatography-Mass Spectrometric Analysis

Gas Chromatography-Mass Spectrometry with Flame Ionization Detection (GC-MS-FID) was performed to comprehensively analyze the chemical components of the extracted crude tall oils (Table 4.4). This method separates compounds through gas chromatography, identifies them via mass spectrometry, and quantifies them with flame ionization detection. This ultimately measures fatty acid methyl esters and other components.

The crude tall oil composition can vary depending on the region and type of wood, as well as other factors like wood storage and pulping (Aro & Fatehi, 2017). Accordingly, Table 4.4 presents the normalized composition of fatty acids in hardwood and softwood crude tall oils. The analysis indicated that the hardwood type had higher levels of palmitic and linoleic acids. Conversely, the softwood type exhibited greater quantities of pinolenic and oleic acids. Conjugated linoleic acids were found in both types of crude tall oils, with softwood having a slightly higher proportion. Whereas stearic acid was detected in hardwood but was absent in the softwood sample.

Table 4.4. Normalized composition of fatty acids in hardwood and softwood crude tall oils

Fatty acids	Carbon chain length	Hardwood crude tall oil (%)	Softwood crude tall oil (%)
Palmitic acid	16:0	9.3	7.9
Pinolenic acid	18:3	5.3	22.4
Linoleic acid	18:2	58.9	34.5
Oleic acid	18:1	12.1	20.9
Conjugated linoleic acid	18:2	10.7	14.3
Stearic acid	18:0	3.7	-

In addition to fatty acids, resin acids, terpenoids, and components of essential oils that could be found in coniferous trees, such as epimanool, sclareol, isopimaral, and dehydroabietal, were identified (Panda, 2013). Moreover, sulfurous acid, dimethyl ester (dimethyl sulfite, $C_2H_6O_3S$), and disulfide dimethyl ($C_2H_6S_2$) were also detected, which aligns with Evdokimov *et al.* (2014) and Fengel D. & Wegener G. (1983) findings. Overall, the GC-MS-FID findings highlight the distinct profiles of fatty acids, resin acids, and sulfur-containing compounds found in extracted crude tall oils.

4.5. Characterization of Raw and Modified Bentonite Clay Adsorbent

The FTIR spectra of bentonite clay before and after HCl activation and iron III impregnation are presented in Figure 4.3. The peak at 3630 cm^{-1} and the broad peak at 3406 cm^{-1} could be attributed to the O-H stretching vibration of the Al-OH groups and the O-H (H-O-H) stretching vibration from hydration of hydroxyl molecules, respectively. The peak at 1637 cm^{-1} was assigned to the bending of O-H bonds of water molecules in the silicate matrix. Peaks at 1087 cm^{-1}, 991 cm^{-1}, 915 cm^{-1}, 878 cm^{-1}, and 799 cm^{-1} were due to stretching vibrations of functional groups Si-O-Al, Si-O-Si, Al-OH-Al, Al-Fe-OH, and Al-Mg-OH, respectively, on tetrahedral and octahedral sheets (Chang *et al.*, 2020; Shattar *et al.*, 2020). The peaks near 799 cm^{-1} confirmed the presence of quartz in the bentonite (Tyagi *et al.*, 2006). A decrease in the intensity of stretching and bending bands could be due to the leaching of octahedral cations, such as Al^{3+} and Mg^{2+}, from the bentonite structure, thus possibly indicating the destruction of the octahedral layer. During the modification process, the protons might have penetrated the bentonite layers to attack the OH groups, altering OH vibration and octahedral cations (Shattar *et al.*, 2020).

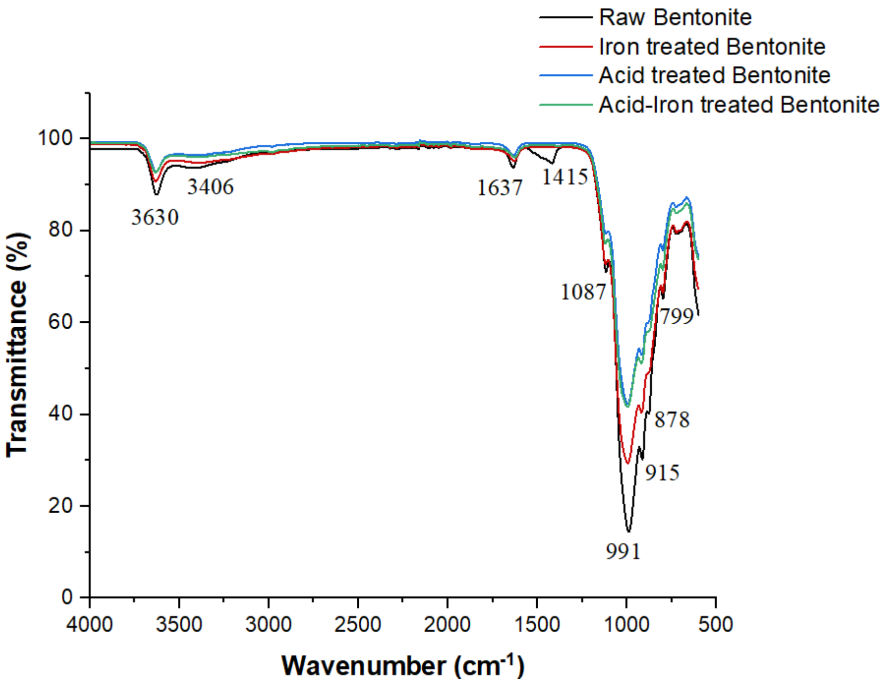


Figure 4.3. Fourier transform infrared spectra of raw and modified bentonite adsorbent

4.6. Analysis of Extractive Desulfurization Using Solvents

4.6.1. Poultry Fat

Extractive desulfurization was performed using various solvents to determine their effectiveness in reducing the sulfur content in poultry fat. The initial sulfur content of poultry fat was 100.0 ± 0.8 ppm. When washed with water, the sulfur content decreased to 91 ± 3 ppm, with acetonitrile 85 ± 3 ppm, with methanol 79.3 ± 0.6 ppm, and with diethylene glycol mono-ethyl ether 76 ± 1 ppm (Figure 4.4).

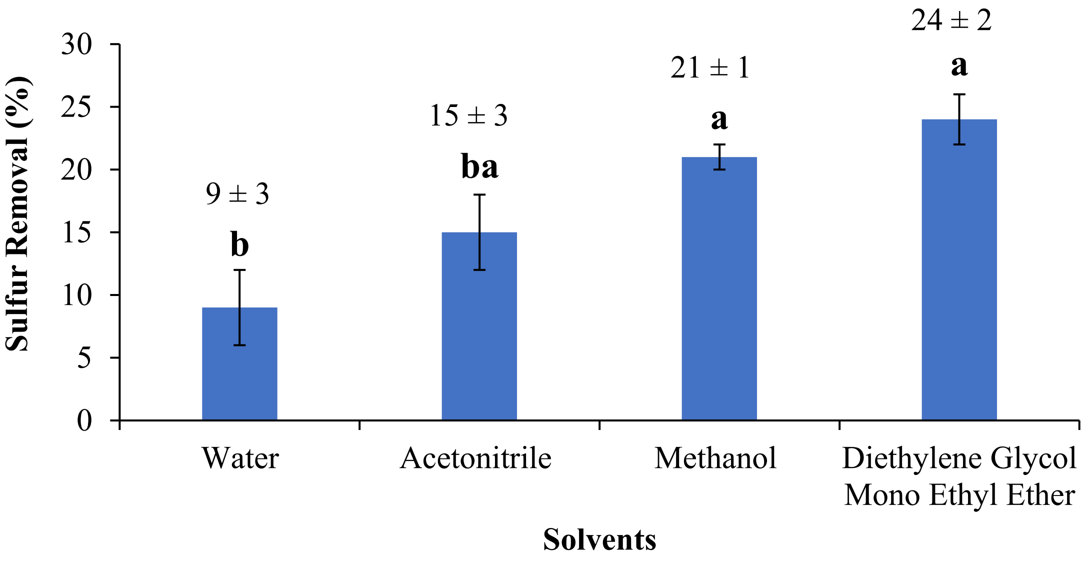


Figure 4.4. Comparison of sulfur removal efficiency across different solvents in poultry fat using ICP-OES

Values are expressed as mean ± standard deviation (n = 3). Different superscript letters (a, ab, b) above bars indicate significant differences between groups at $p < 0.05$. Bars that do not share the same letter are significantly different, the statistical analysis was performed by one-way ANOVA and Tukey's test

Compared to other solvents, water had the lowest sulfur removal efficiency. This could be due to its high polarity, allowing it to dissolve only sulfur compounds with polar functional groups. The limited interaction between water and the hydrophobic lipid structure of poultry fat could have reduced its efficacy in extracting sulfur since nonpolar sulfur compounds in fats do not mix well with water. On the other hand, acetonitrile, a polar aprotic solvent with no hydrogen bonding, possesses a high dielectric constant of 38.8 and a dipole moment of 3.92 D. These properties enable it to dissolve a range of ionic and nonpolar compounds (Alston Steiner & Gordy, 1966). However, it is less reactive than hydroxylic solvents, which contain hydroxyl groups (-OH) such as water and methanol (that can form strong hydrogen bonds) because it weakly solvates most cations and anions (Ramana *et al.*, 2013). Despite those characteristics, there was no significant difference in the percentage of sulfur removal between acetonitrile and methanol. This could be due to the reduced interaction between acetonitrile and non-polar sulfur compounds. Methanol, characterized by a polar protic nature, resulted in significantly greater sulfur extraction from poultry fat when compared to water. This could be due to the formation of hydrogen bonding with sulfur-containing compounds, which could have enhanced its ability to dissolve both polar and moderately non-polar substances. Lastly, diethylene glycol mono ethyl ether removed a higher percentage of sulfur compared to others, except methanol (since no significant difference was observed). This effectiveness could be attributed to its amphiphilic nature, characterized by hydrophobic and hydrophilic properties. These properties may have enabled it to interact with polar and non-polar sulfur compounds.

4.6.2. Brown Grease

This study evaluated the effectiveness of four different solvents for removing sulfur compounds from brown grease: water, acetonitrile, methanol, and diethylene glycol mono ethyl ether using ICP-OES. Initially, the sulfur content in the brown grease was 515 ± 5 ppm. These sulfur compounds likely arise from the degradation and oxidation of sulfur-containing amino acids and proteins in food ingredients during cooking.

Acetonitrile, methanol, and diethylene glycol mono ethyl ether completely dissolved the brown grease. This may be due to their compatibility with polar compounds and non-polar lipid components. It could also be due to the presence of high free fatty acid content in brown grease, which is observed in the HPLC analysis (section 4.10.1). The non-polar portions of solvent molecules may have interacted with the hydrophobic lipid components of the brown grease through van der Waals forces, further promoting dissolution. However, this complete dissolution made it impossible to analyze the sulfur content post-treatment.

As a result, water was used as the only solvent for extracting sulfur compounds because it did not dissolve the brown grease. The sulfur removal efficiency using water was significant, as evidenced by the reduction in sulfur content from 515 ± 5 ppm to 257 ± 3 ppm, corresponding to a sulfur removal percentage of 50 ± 1%. When brown grease was subjected to water washing for sulfur removal, the polar nature of these sulfur compounds may have facilitated their dissolution through hydrogen bonding and dipole-dipole interactions. Water molecules could have formed hydrogen bonds with sulfur-containing functional groups, enhancing their solubility in water. While water effectively dissolved polar sulfur compounds, it did not interact strongly with the non-polar components of brown grease, such as free fatty acids and other lipids. The findings of this study highlight the necessity of choosing appropriate solvents for sulfur removal in feedstocks.

4.6.3. Tall Oil Soap

As discussed in section 3.2.5.2, the sulfur content of the crude tall oils extracted from tall oil soap and treated with water was used as a baseline to determine the percentage removal of sulfur when treated with other solvents such as acetonitrile, methanol, and diethylene glycol mono ethyl ether. The initial sulfur content of the hardwood and softwood crude tall oils was measured to be 1490 ± 40 ppm and 2040 ± 40 ppm, respectively. Hardwood crude tall oils, when washed with acetonitrile, the sulfur content decreased to 1040 ± 20 ppm, with methanol 990 ± 30 ppm, and with diethylene glycol mono-ethyl ether 1070 ± 20 ppm. Whereas, in softwood crude tall oils, when washed with acetonitrile, the sulfur content decreased to 1640 ± 4 ppm, with methanol 1610 ± 20 ppm, and with diethylene glycol mono-ethyl ether 1580 ± 7 ppm. Despite slight variations, these solvents had no significant difference in the sulfur removal efficiencies for both feedstocks (Figures 4.5 and 4.6). The sulfur in hardwood and softwood crude tall oil may have come from sulfur-containing compounds added during the kraft pulping process. Hardwood crude tall oils had lower sulfur content than softwood, this can be explained by Fengel Dietrich & Wegener Gerd, (1983), who demonstrated that hardwoods typically require a lower sulfide charge (15-20%) than softwoods (25-35%) during Kraft pulping process.

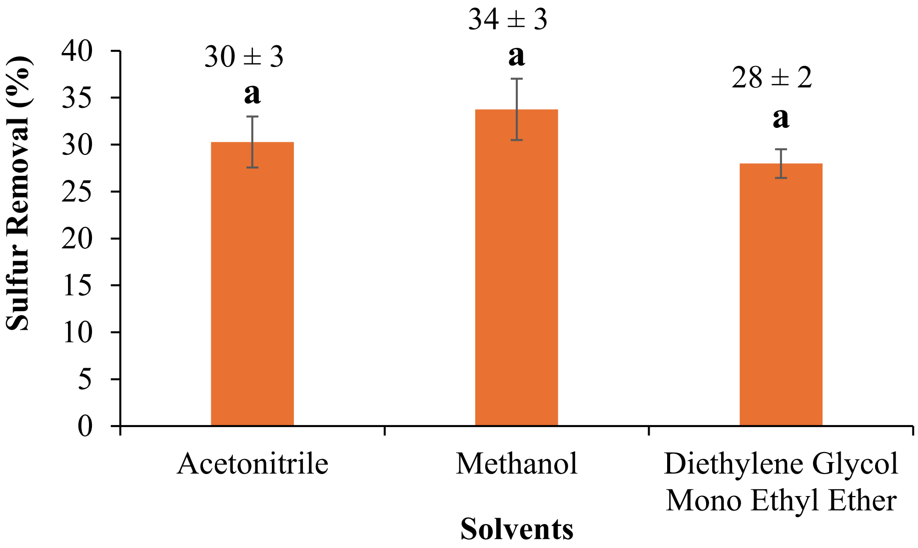


Figure 4.5. Comparison of sulfur removal efficiency across different solvents in Hardwood crude tall oil using ICP-OES

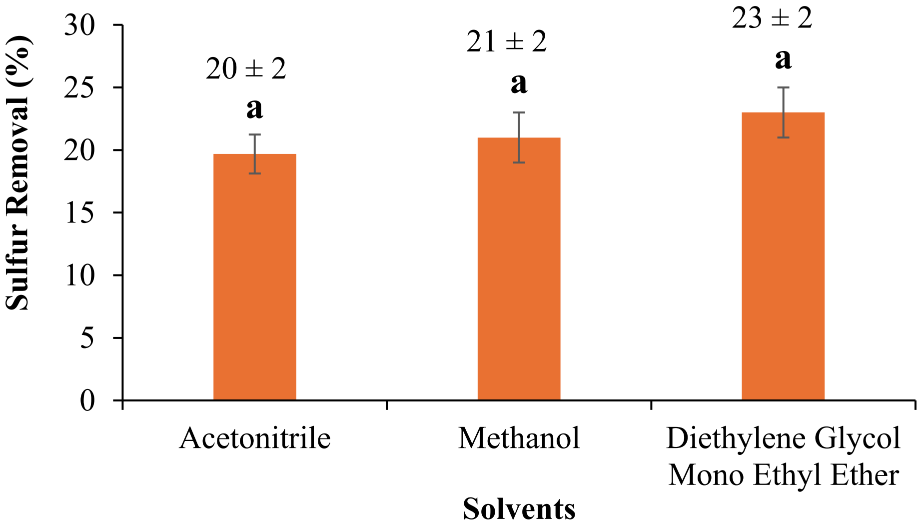


Figure 4.6. Comparison of sulfur removal efficiency across different solvents in Softwood crude tall oil fatty acid

Values are expressed as mean ± standard deviation (n = 3). Different superscript letters (a, b) above bars indicate significant differences between groups at $p < 0.05$. Bars that do not share the same letter are significantly different, the statistical analysis was performed by one-way ANOVA and Tukey's test

Acetonitrile has a partial positive charge on its carbon atom and a partial negative charge on its nitrogen atom. In the same way, the polarity of methanol is due to the strong electronegativity of the oxygen atom attached to hydrogen, resulting in a notable dipole moment. The presence of an oxygen atom between two ethyl groups with varying electronegativities causes the polarity of diethylene glycol mono ethyl ether. Therefore, the outcomes observed could result from a combination of dipole-dipole interactions and hydrogen bonding between polar solvents and sulfur compounds. Even though solvents have different properties, similar outcomes implied that all solvents were equally effective in dissolving and removing sulfur compounds from hardwood and softwood crude tall oil. The difference in the percentage of sulfur removal from crude tall oils of hardwood and softwood could be due to their apparent chemical compositions and structural features. Furthermore, processing conditions, such as temperature and processing time, could also have an effect.

To sum up, the sulfur compounds were successfully removed when washed with different solvents, noting that brown grease was washed with water only. However, sulfur removal from poultry fat through the solvent extraction method was low, possibly due to a polarity difference preventing the sulfur compounds from dissolving properly. Therefore, the coming method employed oxidizing agents before solvent extraction to convert non-polar sulfur compounds into more polar forms. This method aimed to increase the amount of sulfur extracted by improving the selectivity of the sulfur compounds and enhancing their polarity, thus making them easier to extract with the solvents.

4.7. Oxidative Desulfurization

4.7.1. Operating Parameters Effect on Percentage Sulfur Removal

Understanding the impact of operating parameters on the efficiency of oxidative desulfurization was crucial for successfully removing sulfur compounds from poultry fat and brown grease. Hence, key parameters such as temperature, catalyst-oxidant molar ratio, and catalyst-oxidant concentration relative to the feedstock were assessed. Analyzing these factors offered valuable information into the conditions necessary for potentially enhancing the sulfur removal efficiency and improving the overall effectiveness of the oxidative desulfurization process for these intricate feedstocks.

4.7.1.1. Effect of Temperature

The data in Table 4.5 compared the results of two oxidation conditions, one conducted at 90°C and the other at 60°C. Both sets used a fixed ratio of acetic acid to hydrogen peroxide at a molar ratio of 1:3.57 and 36.5% w/w of catalyst-oxidant concentration relative to feedstock. The conditions yielded varying sulfur content reductions and corresponding sulfur removal percentages from poultry fat and brown grease (Table 4.5), with an initial sulfur content of 100.0 ± 0.8 ppm and 515 ± 5 ppm, respectively.

Table 4.5. Effect of temperature on percentage sulfur removal in poultry fat and brown grease at a molar ratio of CH_3COOH: H_2O_2 (1:3.57) and 36.5% w/w of catalyst-oxidant concentration relative to feedstock

Feedstock Used	Initial Sulfur Content (ppm)	Temperature (° C)	Sulfur Content After Treatment (ppm)	Sulfur Removal (%)
Poultry fat	**100.0 ± 0.8**	90	71.7 ± 0.2	28.3 ± 0.6^a
		60	86 ± 2	14 ± 2^b
Brown grease	**515 ± 5**	90	255 ± 4	50.5 ± 0.3^a
		60	265 ± 5	49 ± 1^b

Values are expressed as mean ± standard deviation (n=3)

Numbers in the same column with different superscripted letters are significantly different and the statistical difference was determined by a two-sample t-test ($p<0.05$)

At 90°C, the higher temperature might have accelerated the decomposition of hydrogen peroxide into highly reactive hydroxyl radicals (•OH) through homolytic cleavage of the O-O bond (Di Furia & Modena, 1982). These hydroxyl radicals are potent oxidizing agents capable of abstracting hydrogen atoms from sulfur-containing compounds in poultry fat and brown grease. This may lead to the formation of sulfur oxides or other oxidized sulfur species. According to Lü *et al.* (2006), the increased concentration of hydroxyl radicals at higher temperatures enhances the rate by increasing the molecular collisions and the activation energy of the reaction. Accordingly, this could have promoted the mobility of reactant molecules within the poultry fat and brown grease matrix, resulting in a more efficient sulfur removal process. Furthermore, the diffusion of acetic acid, hydrogen peroxide, and sulfur-containing compounds may have been enhanced with increased thermal energy, resulting in higher accessibility of reactive sites. This could have improved the contact between the oxidizing agent and the sulfur compounds, aiding in the effectiveness of higher sulfur removal efficiency seen at 90 °C.

In contrast, at 60°C, the lower temperature could have reduced the hydrogen peroxide decomposition rate and the generation of hydroxyl radicals. As a result, the concentration of reactive species available for sulfur oxidation could have been reduced compared to the higher temperature condition. Moreover, the observed reduction in percentage sulfur removal could be due to the slower reaction kinetics, which might hinder the mobility or diffusion of acetic acid and hydrogen peroxide. This might have restricted the accessibility of reactive sites within the poultry fat and brown grease. Accordingly, the contact between the oxidizing agent and the sample could have been reduced, leading to the oxidation of fewer sulfur-containing compounds, making the process less efficient. Additionally, the higher temperature may also have promoted the breakdown of larger sulfur-containing molecules into smaller, more reactive species. This could have further enhanced their susceptibility to oxidation. This aspect could have contributed to the higher sulfur removal efficiency observed at 90°C compared to 60°C. This finding was consistent with prior research conducted by Ali *et al.* (2006), which found a 92% decrease in sulfur content with a temperature rise to 50 °C from the initial room temperature. The statistical analysis confirmed a significant difference in brown grease. Additionally, the precision of the measurements, indicated by the narrow confidence intervals and low variances, supported the reliability of the results. In summary, the differences in sulfur removal efficiency under the two temperature conditions may be due to variations in reaction kinetics, mass transfer rates, and the breakdown of sulfur compounds driven by thermal energy.

4.7.1.2. Effect of Catalyst-Oxidant Molar Ratio

Table 4.6 demonstrates the impact of varying acetic acid (CH_3COOH) to hydrogen peroxide (H_2O_2) molar ratio on sulfur removal efficiency. These experiments were conducted for poultry fat and brown grease at 90 °C. It was noticed that the efficiency of sulfur removal in both poultry fat and brown grease improved significantly with an increase in the molar ratio from 1:0.89 to 1:3.57 (CH_3COOH: H_2O_2). The differences in sulfur removal efficiencies between the two feedstocks may have resulted from variations in their compositions, such as differences in fatty acid content, moisture content, and other organic components.

Table 4.6. Effect of molar ratio of CH_3COOH: H_2O_2 on percentage sulfur removal in poultry fat and brown grease at 90 °C

Feedstock Used	Initial Sulfur Content (ppm)	Molar ratio CH_3COOH:H_2O_2	Sulfur Content After Treatment (ppm)	Sulfur Removal (%)
Poultry fat	**100.0 ± 0.8**	1: 0.89	87 ± 2	13 ± 2^b
		1: 3.57	71.7 ± 0.2	28.3 ± 0.6^a
Brown grease	**515 ± 5**	1: 0.89	265 ± 3	48.5 ± 0.2^b
		1: 3.57	255 ± 4	50.5 ± 0.3^a

Values are expressed as mean ± standard deviation (n=3)
Numbers in the same column with different superscripted letters are significantly different and the statistical difference was determined by a two-sample t-test ($p<0.05$)

In the first experiment, where acetic acid and hydrogen peroxide were mixed at a molar ratio of 1:0.89, and a temperature of 90°C, an oxidation reaction crucial for reducing sulfur content in poultry fat and brown grease may have started. Being a weak acid, acetic acid gives away protons (H^+) in the solution, which probably helps with the protonation of sulfur-containing compounds in the feed. This protonation could have made them more likely to undergo oxidation. At the same time, hydrogen peroxide acts as the oxidizing agent, breaking down into water and oxygen. This free oxygen molecule may have interacted with the sulfur compounds containing protons, facilitating their conversion into sulfur oxides or sulfones, thereby effectively reducing the sulfur content in the feed.

In the second experiment, where acetic acid and hydrogen peroxide were mixed in a molar ratio of 1:3.57 at 90°C, several factors could have increased sulfur removal efficiency. One of these could be the higher volume of acetic acid, which may have increased the availability of protons (H+) in the solution. This increased amount of acetic acid may have provided sufficient acidic conditions to protonate sulfur compounds effectively. This could have facilitated their subsequent oxidation. Additionally, changing the reactant ratio might have influenced the generation and concentration of reactive oxygen species. This could have further impacted the overall reaction kinetics of the oxidation reaction. Altering the concentration of reactants could have affected the rate at which sulfur-containing compounds were oxidized. Hence, the molar ratio of acetic acid to hydrogen peroxide could have enhanced the conditions required for the oxidation reaction to occur efficiently, resulting in increased sulfur removal efficiency. Additionally, Zannikos *et al.* (1995), stated that acetic acid can effectively extract oxidized sulfur-containing compounds in a reaction medium as a solvent. In the current study, it was noticed that higher amounts of acetic acid led to an increase in sulfur removal.

Moreover, the nature of sulfur compounds in the sample oils adds another layer of complexity. Different sulfur compounds may exhibit varying reactivity towards oxidation, influenced by factors such as their chemical structure and functional groups. As a result, differences in the sulfur removal percentages among different feedstocks can occur due to the variations in the oxidation efficiency caused by changes in the catalyst-oxidant molar ratio for different sulfur compounds. After assessing the effectiveness of those conditions for sulfur removal, it was found that the molar ratio of CH_3COOH to H_2O_2 at 1:3.57, at a temperature of 90 °C, was the most effective, with a sulfur removal percentage of 28.3%. Consequently, this condition was used for further analysis of oxidative desulfurization in this study.

4.7.1.3. Effect of Catalyst-Oxidant Concentration Relative to Feedstock

Tables 4.7 and 4.8 outline the impact of catalyst-oxidant concentration relative to poultry fat and brown grease (% in w/w) on sulfur removal efficiency. This was conducted at different molar ratios of acetic acid to hydrogen peroxide at 90 °C.

Table 4.7. Effect of catalyst-oxidant concentration relative to poultry fat (% in w/w) on percentage sulfur removal at 90 °C

Initial Sulfur Content (ppm)	Catalyst-oxidant Over Poultry Fat Concentration (% in w/w)	Sulfur Content After Treatment (ppm)	Sulfur Removal (%)
100.0 ± 0.8	25.74	87 ± 2	13 ± 2^{b}
	36.5	71.7 ± 0.2	28.3 ± 0.6^{a}
	51.48	84 ± 1	16 ± 2^{b}
	73	81 ± 4	19 ± 4^{b}

Values are expressed as mean ± standard deviation (n=3)

a-b superscript letters in the same column indicate significant differences ($P<0.05$) and the statistical analysis was performed through one-way ANOVA and Tukey's test

Table 4.8. Effect of catalyst-oxidant concentration relative to brown grease (% in w/w) on percentage sulfur removal at 90 °C

Initial Sulfur Content (ppm)	Catalyst-oxidant Over Brown Grease Concentration (% in w/w)	Sulfur Content After Treatment (ppm)	Sulfur Removal (%)
515 ± 5	25.74	265 ± 3	48.5 ± 0.2^{b}
	36.5	255 ± 4	50.5 ± 0.3^{a}
	51.48	271 ± 1	47.3 ± 0.6^{b}
	73	267 ± 2	48.1 ± 0.8^{b}

Values are expressed as mean ± standard deviation (n=3)

a-b superscript letters in the same column indicate significant differences ($P<0.05$) and the statistical analysis was performed through one-way ANOVA and Tukey's test

While a higher catalyst-oxidant concentration relative to feedstock initially enhanced sulfur removal, a concentration range existed beyond which further increases did not yield proportional improvements in efficiency. This phenomenon could be due to limitations in reactant availability or the saturation of reactive sites on sulfur-containing compounds. An increase in hydrogen peroxide might lead to a corresponding increase in the rate of oxidation reactions, as more oxidizing agents are available to react with sulfur compounds. However, as the reaction progresses, the availability of other reactants, such as sulfur-containing compounds or the acidic medium provided by acetic acid, may become limiting factors. Furthermore, sulfur-containing compounds in the fat may have a finite number of reactive sites available for oxidation. Once these sites are saturated with oxidizing agents, further additions of hydrogen peroxide may not lead to significant increases in sulfur removal. Consequently, beyond a certain point, sulfur removal efficiency may plateau, and additional catalyst-oxidant concentration relative to feedstock may not produce a proportional increase in sulfur removal. Another possible explanation could be the inefficient breakdown of hydrogen peroxide into water and oxygen through thermal decomposition (Dehkordi *et al.*, 2009). Increased amounts of oxidants might have enhanced the decomposition process, resulting in less sulfur being oxidized. Therefore, identifying the ideal concentration range between oxidizing agents and acidic conditions relative to feedstock is crucial for efficiently reducing sulfur content in poultry fat and brown grease. This will maximize yield and minimize resource consumption and potential adverse effects.

In addition to the chemical factors that influenced sulfur removal efficiency, it is essential to consider the impact of mass transfer limitations (Dehkordi *et al.*, 2009). During the oxidation process, sulfur-containing compounds within poultry fat and brown grease must come in contact with the oxidizing agents (acetic acid and hydrogen peroxide) for the reaction to occur. However, in complex matrices like brown grease, the diffusion of reactants through the samples could be hindered by physical barriers or limited accessibility of reactive sites. Variations in catalyst-oxidant concentration relative to feedstock can influence the diffusion dynamics within the poultry fat and brown grease matrix. An ideal ratio may ensure sufficient penetration of the catalyst and oxidizing agent into the substrate. This will enhance the likelihood of encountering sulfur-containing compounds and promote their oxidation. Conversely, imbalanced ratios may result in uneven distribution or inadequate penetration of reactants. This will lead to localized regions with reduced oxidation activity and lower sulfur removal efficiency. Moreover, the viscosity and composition of the poultry fat and brown grease matrix could have impacted the mass transfer dynamics. Higher viscosities or the presence of particulate matter could also affect the diffusion of reactants, further exacerbating mass transfer limitations. Therefore, alongside the chemical factors, the interplay between mass transfer limitations and catalyst-oxidant concentration relative to feedstock could be the reasons for the observed variations in sulfur removal efficiency in complex samples like poultry fat and brown grease.

Based on the analysis, acetic acid and hydrogen peroxide at a molar ratio of 1:3.57 and 36.5% w/w of catalyst-oxidant concentration relative to feedstock achieved the highest percentage of sulfur removal for both poultry fat and brown grease. These conditions proved to be the most effective. Therefore, they were used for future oxidation reaction experiments to ensure effective sulfur removal across the feedstocks.

4.7.2. Analysis of Oxidative Desulfurization

4.7.2.1. Poultry Fat

The process of oxidative desulfurization changes sulfur compounds into sulfone and sulfoxide derivatives with increased polarity (Campos-Martin *et al.*, 2010; Chandra Srivastava, 2012). Thus, these oxidation products were extracted more easily by polar solvents. The starting sulfur concentration of poultry fat was 100.0 ± 0.8 ppm. After treatment, the sulfur content decreased to 71.7 ± 0.2 ppm when washed with water, 64 ± 2 ppm with acetonitrile, 56 ± 2 ppm with methanol, and 54 ± 2 ppm with diethylene glycol mono ethyl ether (Figure 4.7).

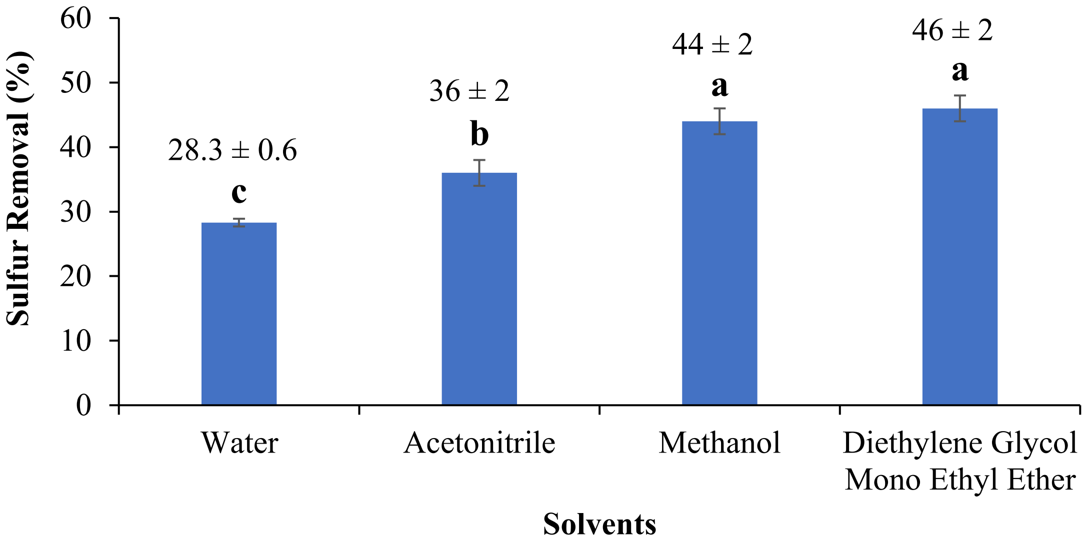


Figure 4.7. Comparison of sulfur removal efficiency during oxidative desulfurization of poultry fat followed by solvent extraction using ICP-OES

Values are expressed as mean ± standard deviation (n = 3). Different superscript letters (a, b, c) above bars indicate significant differences between groups at $p < 0.05$. Bars that do not share the same letter are significantly different, the statistical analysis was performed by one-way ANOVA and Tukey's test

The ANOVA analysis showed a notable variation in sulfur removal effectiveness between the solvents. The Tukey HSD test provided additional insights into these variations, indicating significant differences among most solvents, apart from methanol and diethylene glycol mono ethyl ether. They did not display a significant distinction. This similarity indicated that methanol and diethylene glycol mono ethyl ether had comparable effectiveness in removing the oxidized sulfur compounds from poultry fat. However, water and acetonitrile had lower efficiencies.

Poultry fat contains non-polar components within its complex mixture. According to the results observed, poultry fat was susceptible to oxidation. This could be due to the presence of unsaturated fatty acids, which are more prone to oxidation (Bravo-Lamas *et al.*, 2018). As evidenced by Sohail *et al.* (2022), poultry fat primarily contains oleic acid as its monounsaturated fatty acid and linoleic as a polyunsaturated fatty acid.

Being highly polar, water may not have interacted with the non-polar matrix of poultry fat as effectively as the other organic solvents did. This could have been the reason for its lower efficiency. In addition, the high viscosity of poultry fat could have also hindered the effective blending and interaction of water with the fat. This might have restricted the contact between water and the sulfur compounds, leading to decreased extraction efficiency. Acetonitrile, a polar aprotic solvent, has partial charges on its nitrogen and carbon atoms. This potentially could have facilitated dipole-dipole interactions with the oxidized sulfur compounds, leading to a moderate extraction efficiency. Although acetonitrile is a very polar solvent with a high dipole moment; it was not as effective as methanol in solvating and interacting with sulfur compounds. This may be due to its lack of ability to engage in hydrogen bonding. According to C. Lee *et al.* (1988), methanol can create three hydrogen bonds, with two acting as proton acceptors (using lone pair electrons on oxygen) and one as a proton donor. Methanol, a polar protic solvent, has a hydroxyl group (-OH), which could have allowed it to form stronger hydrogen bonds with oxidized sulfur compounds. Additionally, the significant dipole moment of methanol, caused by the oxygen atom's strong electronegativity when bonded to hydrogen, may have increased its capacity to create hydrogen bonds with the oxidized sulfur compounds. This could have resulted in improved sulfur removal efficiency. Moreover, the smaller size and greater hydrophilicity of methanol may have aided in better penetration and bonding with the sulfur compounds. Due to an oxygen atom sandwiched between two ethyl groups of varying electronegativities, the polarity of diethylene glycol mono ethyl ether could have allowed it to extract oxidized sulfur compounds efficiently. Furthermore, the sulfur compounds in poultry fat might have had better interaction with the functional groups in diethylene glycol mono ethyl ether than with other solvents. This implied that the oxidized sulfur compounds could be more attracted to diethylene glycol mono ethyl ether.

4.7.2.2. Brown Grease

Brown grease was fully dissolved by acetonitrile, methanol, and diethylene glycol mono ethyl ether. Hence, water was the only solvent used for extracting sulfur compounds following the oxidation process (refer to section 4.6.2). In the process of oxidative desulfurization, sulfur compounds were anticipated to transform into more polar varieties, like sulfoxides and sulfones, that can be extracted more easily using polar solvents (Campos-Martin *et al.*, 2010; Chandra Srivastava, 2012). The data in Table 4.9 shows that the percentage sulfur elimination for unoxidized and oxidized brown grease was comparable, exhibiting approximately 50% removal.

Table 4.9. Sulfur removal percentages in oxidized and unoxidized brown grease washed with water

Initial Sulfur Content (ppm)	Treatment Conditions	Sulfur Content After Treatment (ppm)	Sulfur removal (%)
515 ± 5	Unoxidized Brown Grease	257 ± 3	50 ± 1^{a}
	Oxidized Brown Grease	255 ± 4	50.5 ± 0.9^{a}

Values are expressed as mean ± standard deviation (n=3)

Numbers in the same column with different superscripted letters are statistically the same and the statistical difference was determined by a two-sample t-test ($p<0.05$)

The absence of a notable distinction between water-washed and oxidized brown grease in sulfone extraction may have resulted from the brown grease reaching a saturation point in oxidation. This suggested that the brown grease might already have reached a point where additional oxidation did not greatly increase sulfone formation. This highlighted that effective extraction may have occurred just by washing with water. On the other hand, the comparable sulfur removal indicated that the oxidation procedure may not have significantly changed the properties of sulfur compounds in brown grease, underscoring the requirement for more precise desulfurization approaches considering the specific sulfur compounds found in these raw materials. This may also be due to the type of sulfur compounds found in brown grease. Moreover, sulfur removal efficiency could have been greatly influenced by the interaction of sulfur compounds with the washing solvent employed. If the oxidized sulfur compounds did not have a much higher solubility in the washing solvent (water) than their unoxidized counterparts, the removal efficiency would not have significantly improved. The complicated composition of brown grease, as it is a trap grease from various sources, may also have prevented oxidizing agents from reaching the sulfur compounds. Therefore, this could have reduced the effectiveness of oxidation.

4.7.2.3. Extracted Crude Tall Oil

Oxidative desulfurization was impossible for crude tall oils as they solidified when solvents were added after oxidation. According to Gas Chromatography-Mass Spectrometric Analysis, extracted crude tall oil comprised different types of fatty acids, such as oleic, linoleic, and palmitic acids, as well as a variety of resin acids, such as abietic, dehydroabietic (see section 4.4.3), and levopimaric and neoabietic acids (P. Liu *et al.*, 2020). These components may have impacted their behavior during oxidation and solvent-washing procedures. Each component possessed unique chemical characteristics, such as melting points, solubility in solvents, and reactivity to oxidizing agents. Resin acids could have played a role in the solidification because they had higher melting points than typical fatty acids. Abietic acid, for instance, has a melting point of approximately 173 °C, whereas levopimaric acid, neoabietic acid, and dehydroabietic acid melt at 150 °C, 167 °C, and 171 °C, respectively. On the other hand, oleic acid has a melting point of approximately 13-16 °C. When polar solvents were added after oxidation, the higher melting point components might have separated out as the temperature was not high enough to keep them in a liquid state. However, if the resin acids had been eliminated from the crude tall oil beforehand, oxidative desulfurization followed by solvent extraction might have been achievable. Due to these difficulties, the sulfur content analysis of extracted crude tall oils was not carried out.

The oxidative desulfurization method followed by solvent washing effectively reduced the sulfur content of poultry fat significantly. However, lots of sulfur still existed in the sample. Moreover, the sulfur content of oxidized brown grease did not show a marked difference compared to the unoxidized. This indicated that the complicated composition of poultry fat and brown grease may have hindered the effective mixing between the oxidizing agents and the washing solvents. This could have resulted in the observed removal efficiency. To address this challenge, another approach that incorporated ultrasonication was employed. The ultrasonic-assisted oxidative desulfurization method aimed to overcome the constraints observed in conventional oxidative desulfurization. This could be due to the utilization of the mechanical and chemical effects of sound energy. This was expected to improve the interaction between the oxidizing agents and the complex sample matrix, ultimately leading to increased sulfur removal percentages.

4.8. Ultrasonic-Assisted Oxidative Desulfurization

4.8.1. Poultry Fat

The study aimed to evaluate the effectiveness of ultrasonic-assisted oxidative desulfurization for removing sulfur from poultry fat. This method also assessed the effectiveness of various solvents in eliminating sulfur from oxidized poultry fat. The poultry fat initially had a sulfur content of 100.0 ± 0.8 ppm. After treatment, the sulfur content decreased to 21.1 ± 0.3 ppm when washed with water, 22.6 ± 0.2 ppm with acetonitrile, 24.4 ± 0.2 ppm with methanol, and 21.26 ± 0.04 ppm with diethylene glycol mono ethyl ether (Figure 4.8).

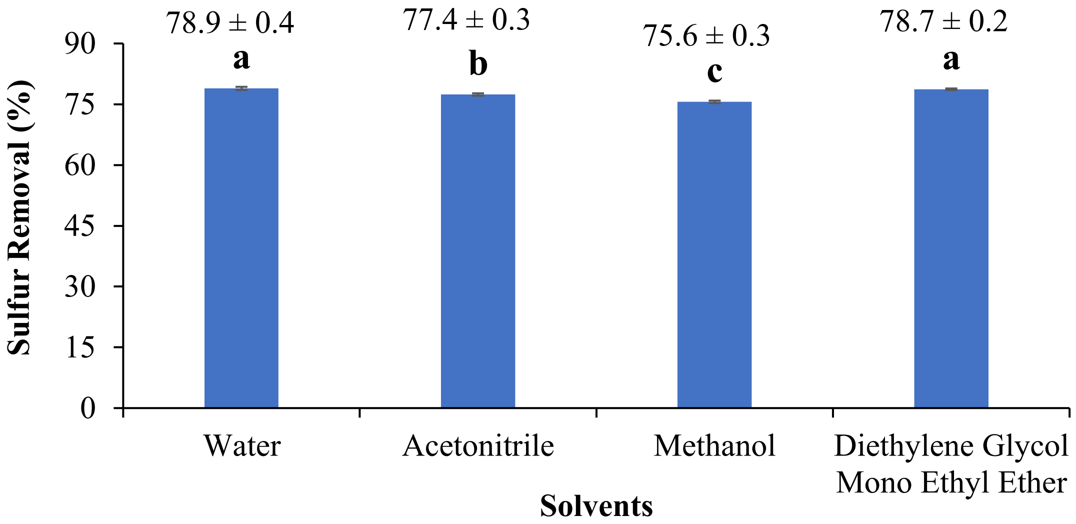


Figure 4.8. Comparison of sulfur removal efficiency during ultrasonic-assisted oxidative desulfurization of poultry fat followed by solvent extraction using ICP-OES

Values are expressed as mean ± standard deviation (n = 3). Different superscript letters (a, b, c) above bars indicate significant differences between groups at $p < 0.05$. Bars that do not share the same letter are significantly different, the statistical analysis was performed by one-way ANOVA and Tukey's test

The ANOVA test results indicated significant differences in the effectiveness of sulfur removal between the solvents. Specifically, methanol was significantly less efficient in removing sulfur than other solvents. Water and diethylene glycol mono ethyl ether demonstrated equal effectiveness, with no significant difference between them. Acetonitrile was also observed to be effective but to a slightly lesser extent than water and diethylene glycol mono ethyl ether.

Incorporating ultrasonic waves into the oxidative desulfurization of poultry fat greatly enhanced the effectiveness of sulfur removal across different solvents. Ultrasonication potentially could have improved the breakdown of sulfur compounds due to the cavitation effects. The process of cavitation, in which tiny bubbles are created and then burst, might have led to the creation of very reactive molecules, such as hydroxyl radicals, due to the increased temperature and pressure in localized areas. These radicals might have enhanced the reaction rates and mass transfer, improving contact between oxidizing agents and sulfur compounds (Choi *et al.*, 2014; Khodaei *et al.*, 2017, 2018). Bolla *et al.* (2012), suggested that ultrasonic-assisted oxidative desulfurization enhances interfacial area through fine emulsion. Moreover, according to Lin *et al.* (2020), higher temperatures can speed up the degradation of carbon-carbon and carbon-sulfur bonds, decreasing the size and complexity of high-molecular sulfur compounds. As a result, the sulfones produced were easily extracted with polar solvents, possibly explaining the improved desulfurization effectiveness seen in this method. Similarly, Hosseini & Hamidi *et al.*, (2014) demonstrated the efficacy of combined oxidative desulfurization and ultrasonic approach in removing sulfur from crude oil, with acetic acid exhibiting the highest desulfurization efficiency followed by formic acid and propionic acid. Additionally, their study found ultrasonic-assisted oxidative desulfurization to achieve approximately 30% higher desulfurization rates compared to mechanically stirred oxidative desulfurization.

4.8.2. Brown Grease

Solvents such as acetonitrile, methanol, and diethylene glycol mono ethyl ether were tested for their efficiency in removing sulfur compounds. However, as discussed in section 4.6.2, these solvents completely dissolved the brown grease. Hence, water was the only solvent used for extracting sulfur compounds following the ultrasonic-assisted oxidative desulfurization process.

During this process, sulfur compounds were anticipated to transform into more polar varieties, like sulfoxides and sulfones, that could be extracted more easily using polar solvents. However, the data in Table 4.10 shows that the percentage of sulfur elimination for unoxidized and ultrasound-assisted oxidized brown grease was comparable. Both methods exhibited approximately 50% removal.

Table 4.10. Sulfur removal percentages in ultrasound-assisted oxidized and unoxidized brown grease washed with water

Initial Sulfur Content (ppm)	Treatment Conditions	Sulfur Content After Treatment (ppm)	Sulfur removal (%)
515 ± 5	Unoxidized Brown Grease	257 ± 3	50 ± 1^a
	Ultrasound-assisted Oxidized Brown Grease	261 ± 5	49 ± 1^a

Values are expressed as mean ± standard deviation (n=3)

Numbers in the same column with different superscripted letters are statistically the same and the statistical difference was determined by a two-sample t-test ($p<0.05$)

The absence of a notable distinction between water-washed brown grease and ultrasound-assisted oxidized brown grease in sulfone extraction may have resulted from the brown grease reaching a saturation point in oxidation. This suggested that the brown grease could already have reached a point where additional oxidation did not greatly increase sulfone formation. This highlighted effective extraction could occur just by washing with water. Therefore, the comparable sulfur removal indicated that the oxidation procedure may not have significantly changed the properties of sulfur compounds in brown grease. This underscored the requirement for more precise desulfurization approaches considering the specific sulfur compounds found in these raw materials. Moreover, sulfur removal efficiency could have been greatly influenced by the interaction of sulfur compounds with the washing solvent employed. If the oxidized sulfur compounds did not have a much higher solubility in the washing solvent (water) than their unoxidized counterparts, the removal efficiency would not have significantly improved. The complicated composition of brown grease, as it is a trap grease from various sources, may also have prevented oxidizing agents from reaching the sulfur compounds. therefore, this could have reduced the effectiveness of oxidation.

4.9. Ultrasonic-Assisted Adsorptive Desulfurization

4.9.1. Poultry Fat

This study evaluated the effectiveness of various adsorbents in removing sulfur from poultry fat. Initially, the poultry fat had a sulfur content of 100.0 ± 0.8 ppm. Following the treatment, the sulfur content in the poultry fat decreased to 93 ± 1 ppm when using raw bentonite, 92 ± 4 ppm with iron-impregnated bentonite, 95 ± 1 ppm with bentonite treated with 0.1 M HCl, and 97 ± 2 ppm with 0.1 M HCl-Fe-impregnated bentonite. Amberlyst®-A21, an anionic resin, lowered the sulfur content to 90 ± 2 ppm, whereas Amberlite®-IRC50, a cationic resin, decreased it to 93 ± 2 ppm. The highest reduction was achieved with Al-MCM-41, bringing the sulfur content down to 62 ± 2 ppm (Figure 4.9).

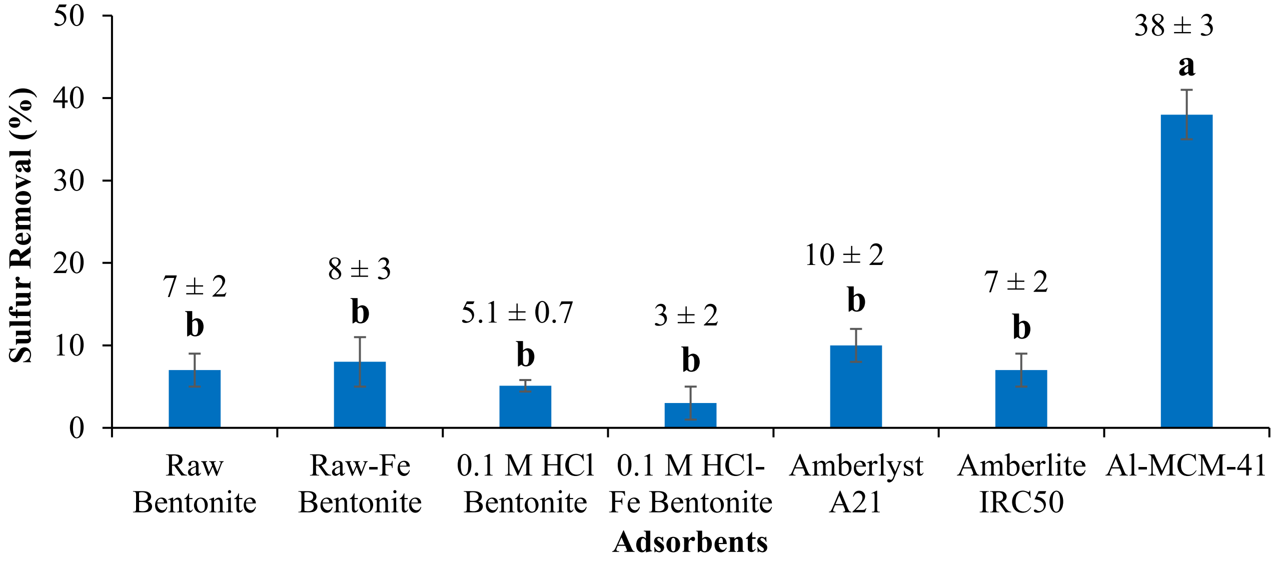


Figure 4.9. Comparison of sulfur removal efficiency across various adsorbents in poultry fat using ICP-OES

Values are expressed as mean ± standard deviation (n = 3). Different superscript letters (a, b) above bars indicate significant differences between groups at $p < 0.05$. Bars that do not share the same letter are significantly different, the statistical analysis was performed by one-way ANOVA and Tukey's test

The ANOVA analysis confirmed that Al-MCM-41 performed better than the other adsorbents in removing sulfur. The Tukey HSD test also indicated that the sulfur elimination by Al-MCM-41 was significantly different from that of the other adsorbents. In contrast, the efficiencies of the other adsorbents did not differ from one another. The increased sulfur removal observed with Al-MCM-41 may be due to its high surface area and mesoporous structure, which might have provided active sites for adsorption. The large pore volume and unique surface chemistry of Al-MCM-41 could have also facilitated the adsorption of sulfur compounds more effectively than the other adsorbents tested. However, even though Al-MCM-41 removed the sulfur compounds effectively, it was difficult to separate them from the feed, which could be due to their fine particulate form.

Iron was successfully impregnated into raw bentonite clay, as evidenced by initial and post-treatment analyses of iron solution. The raw bentonite adsorbed 60% of the iron, while the acid-activated bentonite adsorbed 70%. This indicated that HCl washing could have potentially improved iron insertion by washing out some metals from the bentonite's surface and increasing active sites. However, despite higher iron deposition, the sulfur removal efficiency of iron-impregnated bentonite was similar to that of raw bentonite.

According to Azzouz *et al.* (2006), Bentonite is a microporous clay. These adsorbents' lower sulfur removal efficiencies might be due to their comparatively smaller surface areas and less efficient pore structure. As a result, larger sulfur molecules may experience limitations in fitting the available surface sites due to steric hindrance. As a result, this could explain their limited effectiveness. Another reason might be the nature of sulfur compounds found in the poultry fat, as they may not possess suitable surface or chemical interactions with the bentonite clays, leading to ineffective adsorption. Shen, (2001) has mentioned that Bentonite has a hydrophilic surface, which could have made it inefficient in adsorbing hydrophobic sulfur compounds due to its affinity for polar substances. On the other hand, Amberlyst®-A21 performed slightly better than Amberlite®-IRC50. This may be attributed to variations in their ion-exchange capacities and the types of functional groups used in the adsorption mechanism. The sulfur compounds' ability to interact with the functional groups on these resins could have impacted their varying effectiveness.

4.9.2. Brown Grease

This study evaluated the effectiveness of various adsorbents in removing sulfur from brown grease. Initially, brown grease had a sulfur content of 515 ± 5 ppm. After treatment, the sulfur contents were changed as follows: raw bentonite (304 ± 5 ppm), iron-treated bentonite (304 ± 7 ppm), bentonite treated with 0.1 M HCl (307 ± 8 ppm), iron-treated bentonite with 0.1 M HCl (303 ± 2 ppm), Amberlyst®-A21 (300 ± 7 ppm), Amberlite®-IRC50 (301 ± 3 ppm), and Al-MCM-41 (280 ± 8 ppm) (Figure 4.10).

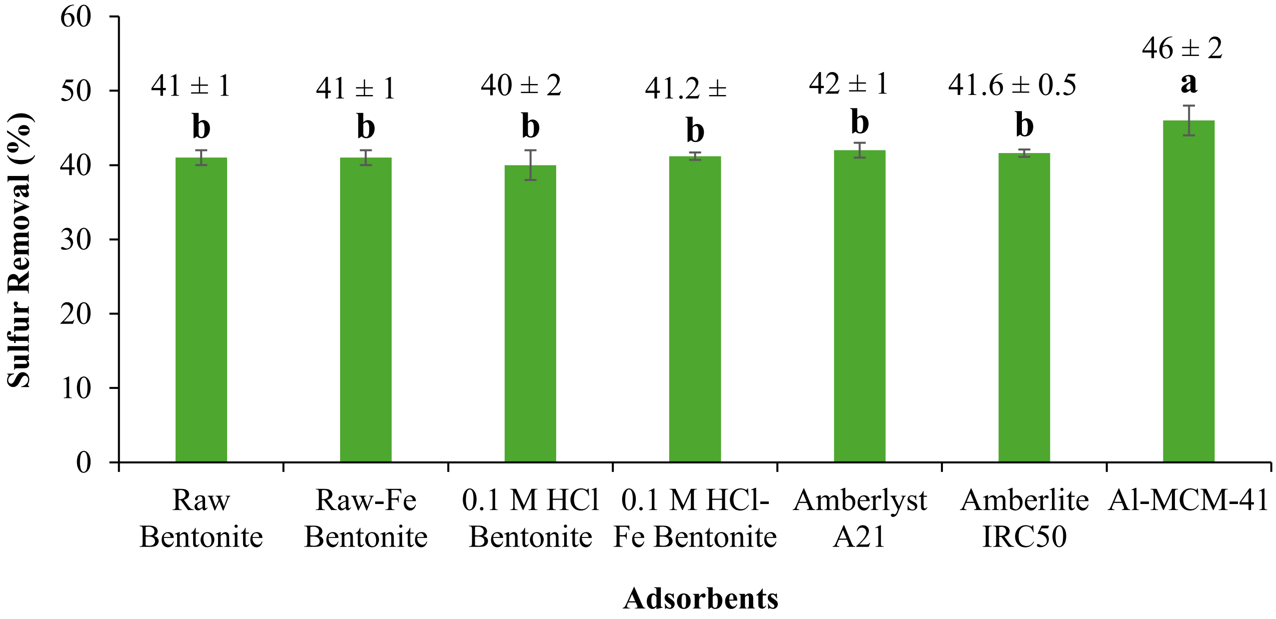


Figure 4.10. Comparison of sulfur removal efficiency across various adsorbents in brown grease using ICP-OES

Values are expressed as mean ± standard deviation (n = 3). Different superscript letters (a, b) above bars indicate significant differences between groups at $p < 0.05$. Bars that do not share the same letter are significantly different, the statistical analysis was performed by one-way ANOVA and Tukey's test

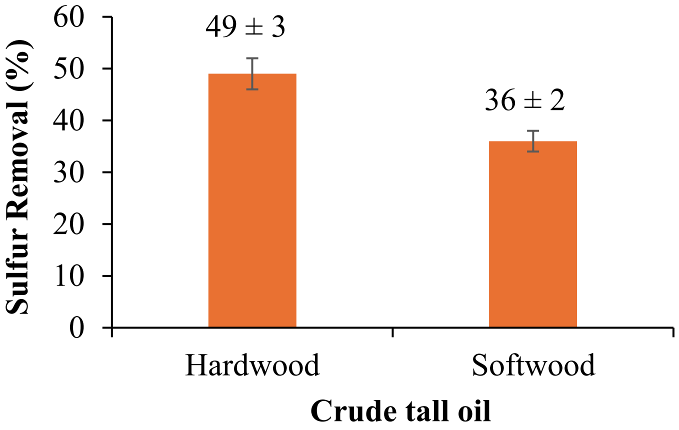
According to the ANOVA analysis and Tukey HSD test, Al-MCM-41 showed significantly higher sulfur removal efficiency compared to the other adsorbents. This may be due to its mesoporous structure. This offers a greater surface area, pore volume, and more available adsorption sites. This might have led to enhanced sulfur adsorption. Just like the problem faced with poultry fat, although Al-MCM-41 successfully removed sulfur compounds, separating them from brown grease was challenging because they were in a very fine particulate form.

The other adsorbents (bentonite and resins) exhibited satisfactory results, achieving approximately 40-42% sulfur removal. However, even after being activated with HCl and modified with iron, bentonite clay did not show improvement in sulfur removal. This could be due to the nature of sulfur compounds in the brown grease, which may not have had sufficient interaction with the modified surfaces of bentonite. As mentioned by Shen, (2001), Bentonite has a hydrophilic surface, which could have made it effective in adsorbing hydrophilic sulfur compounds due to its affinity for polar substances. However, this could have made it inefficient in adsorbing hydrophobic sulfur compounds. Moreover, bentonite is a microporous clay (Azzouz *et al.*, 2006); its surface area might have been limited to adsorb larger molecular-sized sulfur compounds, which could explain the observed efficiency. The similar effectiveness in removing sulfur from brown grease using anionic (Amberlyst®-A21) and cationic (Amberlite®-IRC50) resins may be attributed to their charges influencing their ability to exchange ions with sulfur compounds.

4.9.3. Extracted Crude Tall Oils

The sulfur removal efficiencies for all adsorbents tested in the previous two feeds were comparable, except Al-MCM-41. However, Al-MCM-41 encountered challenges in its separation from the previous feed and was, therefore, not suitable for processing crude tall oils. This study was conducted for extracted crude tall oils, which are more viscous and impure (presence of resins) than poultry fat and brown grease. Thus, only raw bentonite adsorbent was utilized to desulfurize hardwood and softwood crude tall oils.

As mentioned in section 3.2.5.2, the sulfur contents in crude tall oils obtained from tall oil soap and treated with water were used as a reference point to evaluate the effectiveness of sulfur removal by raw bentonite. The initial sulfur content in the extracted crude tall oil was 1490 ± 40 ppm for hardwood and 2040 ± 40 ppm for softwood. Following raw bentonite treatment, sulfur content decreased to 760 ± 30 ppm and 1300 ± 20 ppm, respectively (Figure 4.11).



Values are expressed as mean ± standard deviation (n = 3).

Figure 4.11. Sulfur removal efficiency in crude tall oils using bentonite clay adsorbent through ICP-OES

Both types of crude tall oils displayed significant sulfur reduction when treated with raw bentonite. However, the sulfur removal efficiency for hardwood crude tall oil was higher than for softwood. This could possibly be due to the differences in sulfur compound characteristics and variations in crude tall oil chemical compositions. According to Lingaiah *et al.* (2005), Bentonite clay is mostly composed of montmorillonite, a cationic clay mineral that could have enabled it to adsorb anionic sulfur compounds. Similarly, Mockovčiaková *et al.* (2009) mentioned the good adsorption ability of bentonite clay comes from its negative charge which can be neutralized by the adsorption of positively charged anions. Moreover, bentonite is a microporous clay (Azzouz *et al.*, 2006); its surface area might have been limited to adsorb larger molecular-sized sulfur compounds, which could be the reason for its limited effectiveness. As mentioned by Shen, (2001) Bentonite's hydrophilic surface could have made it effective in adsorbing hydrophilic sulfur compounds due to its affinity for polar substances. However, this could have made it inefficient in adsorbing hydrophobic sulfur compounds.

To summarize, the ultrasonic assisted-adsorptive desulfurization method was employed to remove sulfur compounds from poultry fat, brown grease and extracted crude tall oils. The results indicated that understanding the adsorbents' properties and their interaction with the sulfur compounds in the feeds will allow for better selection and enhancement of adsorbents in sulfur removal procedures. These insights suggest further exploration and improvement of desulfurization methods and materials.

4.10. Evaluating Sulfur Removal During the Thermochemical Conversion of Lipids into Diesel-Equivalents

4.10.1. High-Performance Liquid Chromatography Analysis of Acyl Glycerol Composition

The composition of acylglycerol and free fatty acids in poultry fat and brown grease before and after hydrolysis was analyzed using HPLC-ELSD. This analysis provided insights into the extent of hydrolysis of triacylglycerols (TAG), diacylglycerols (DAG), and monoacylglycerols (MAG) into free fatty acids (FFA). This helped to determine the efficiency of the hydrolysis process and identify the chemical transformations occurring within the samples.

The initial TAG content in poultry fat was 70 ± 2%, suggesting a high proportion of intact triacylglycerides. Following the first hydrolysis, the TAG content was substantially reduced to 14.1 ± 0.9%, indicating extensive hydrolysis. This reduction suggested that the hydrolysis process effectively broke down triacylglycerols into simpler components such as DAG, MAG, and FFA, resulting in increased values of 19 ± 1%, 7 ± 1%, and 67 ± 3%, respectively. After the second hydrolysis, the TAG content slightly increased to 17.9 ± 0.5%, possibly due to the reformation of TAGs from DAGs and MAGs or the presence of unreacted triacylglycerols. At the same time, the FFA content further increased to 82 ± 1%, confirming the efficiency of the second hydrolysis process (Figure 4.12).

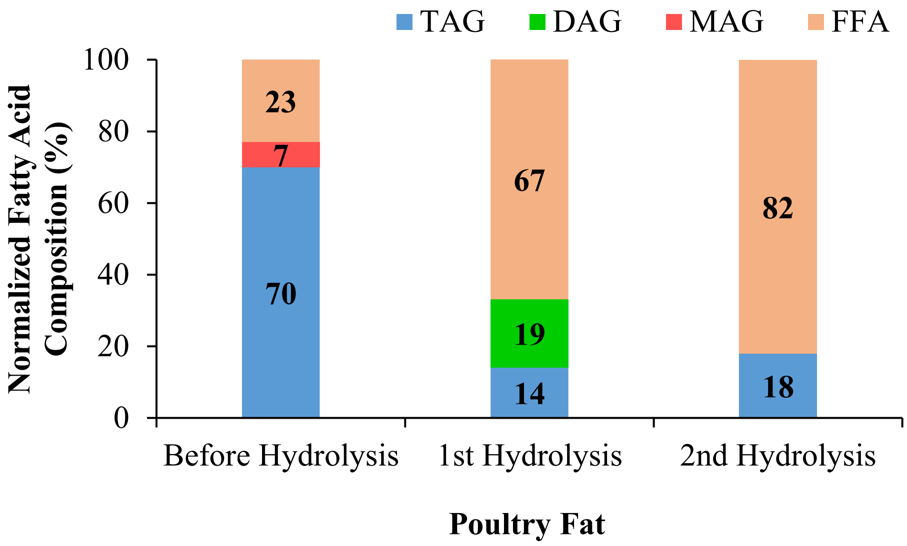
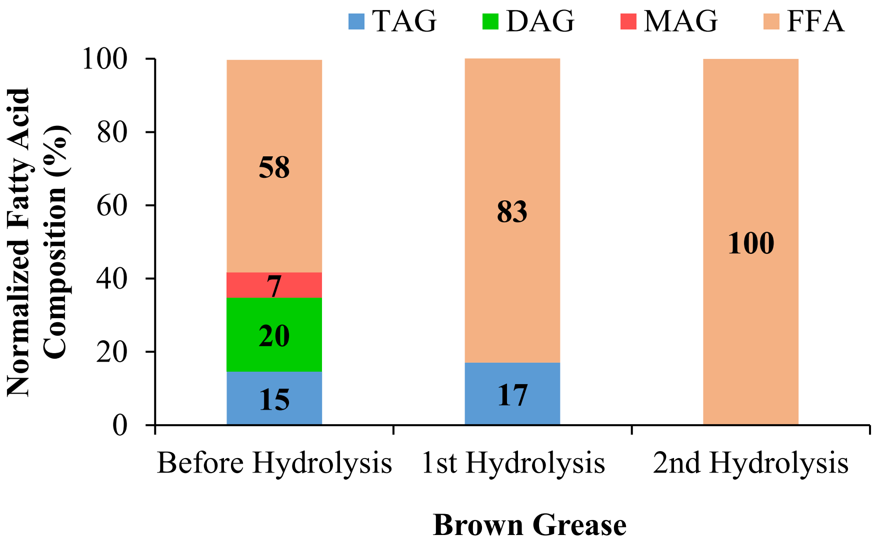


Figure 4.12. Normalized Fatty Acid Composition of Poultry Fat using HPLC

The initial TAG content of brown grease was 14.6 ± 0.2%, indicating a lower proportion of intact triacylglycerols compared to poultry fat. This might have been due to the prolonged exposure of brown grease to heat, moisture, and microbial activity in grease traps. This could lead to partial hydrolysis before the experimental process. The DAG, MAG, and FFA contents were observed to be 20.2 ± 0.4%, 6.9 ± 0.1%, and 58 ± 2%, respectively, reflecting that a substantial portion of the triacylglycerols had already been hydrolyzed into smaller components. This closely aligns with the findings reported by Spiller *et al.* (2020), who examined brown grease and obtained a 61 ± 4% FFA content in their study. Ward, (2012) also notes that the combination of oils, fats, and greases undergo considerable hydrolysis, resulting in the conversion of these substances into free fatty acids. This further supported the notion that brown grease undergoes extensive hydrolysis before any treatment. However, high levels of free fatty acids (FFAs) can significantly reduce the oxidative stability of oils, negatively impacting their shelf life (Lam *et al.*, 2010). Following the first hydrolysis, the TAG content increased to 17.1 ± 0.4%, due to the reformation of TAGs from DAGs and MAGs or the presence of unreacted triacylglycerides. The FFA content increased to 83 ± 1%, indicating further hydrolysis of the remaining glycerol. After the second hydrolysis, the FFA content reached 100 ± 3%, reflecting complete hydrolysis or complete conversion of triacylglycerols (Figure 4.13).



TAG: Triacylglycerol, **DAG:** Diacylglycerol, **MAG:** Monoacylglycerol, **FFA:** Free fatty acids

Figure 4.13. Normalized Fatty Acid Composition of Brown Grease using HPLC

The systematic approach of conducting two hydrolysis steps maximized the conversion of fats into simpler forms for the upcoming pyrolysis process. Removing glycerol after the first hydrolysis and adding fresh water for the second hydrolysis facilitated the breakdown of any remaining triacylglycerols, achieving higher conversion. The differences in the initial compositions of poultry fat and brown grease influenced the extent of hydrolysis and the resulting product distribution. With its higher initial TAG content, poultry fat underwent substantial hydrolysis, as evidenced by the considerable increase in FFA content. In contrast, brown grease, already partially hydrolyzed due to its environmental exposure, exhibited a higher initial FFA and lower TAG content.

These findings underscore the effectiveness of the hydrolysis process in converting fats/oils into free fatty acids, a crucial step for subsequent diesel production and sulfur removal. The processes might also play a vital role in weakening and breaking the bonds of sulfur compounds when exposed to extreme conditions. The reduction in TAG content and the corresponding increase in FFA content during hydrolysis confirmed the process's efficiency. The observed variations in poultry fat and brown grease composition highlight the importance of feedstock characteristics on hydrolysis efficiency.

4.10.2. Assessing Sulfur Removal Efficiency during Hydrolysis Process

The hydrolysis process converts triacylglycerols into glycerol and free fatty acids in the presence of water at high temperatures and pressures. During the initial hydrolysis of poultry fat, there was a 7.3% increase in sulfur content, likely resulting from the breakdown of triacylglycerols, which may release sulfur-containing compounds that were originally bound to the fatty acids. However, in the second hydrolysis, a reduction of 10.5% in sulfur content was observed, possibly due to the removal of glycerol. In contrast, during the hydrolysis of brown grease, sulfur compounds were potentially broken down or removed, leading to an initial decrease in sulfur content of 45%. Further breakdown in the second stage contributed to a continued reduction of 19%. Brown grease, being a byproduct of cooking processes, may contain sulfur compounds from food residues or additives, which may be disrupted during hydrolysis, possibly contributing to the decrease in sulfur content. The observed variation in sulfur content during hydrolysis stages might have been influenced by factors such as temperature, feedstock composition, and water content.

When water temperature rises, its polarity decreases. As a result, non-polar organics become more soluble, while polar organics become less soluble (Fernández-Prini *et al.*, 1991). Subcritical water's lower dielectric constant with increasing temperature, compared to ambient water, may have aligned the polarity of water and oil. This could have made it an efficient medium for reactions with non-polar substances oil (Carr *et al.*, 2011; H & McClain, 1949; Kruse & Dinjus, 2007). According to Fernández-Prini *et al.* (1991), when the water temperature rises above 100 °C, its dielectric constant becomes comparable to that of organic solvents such as DMSO at room temperature. Therefore, water under subcritical conditions plays a dual role in hydrolysis as both a reactant and a solvent (King *et al.*, 1999; Pinto & Lanças, 2006). At lower temperatures, hydrogen bonds exhibit greater strength, increasing the dielectric constant value (Nakahara *et al.*, 2001). When the water temperature rises, the stronger thermal movement could have weakened each hydrogen bond, resulting in a larger decrease in the dielectric constant value (Caffarena & Grigera, 2004). Decreased hydrogen bonding strength and water polarity may have resulted in greater solubility of hydrophobic organic compounds in water (Carr *et al.*, 2011).

Additionally, free fatty acids formed during the hydrolysis reaction of fats/oils can act as acid catalysts, speeding up their own reaction (Alenezi *et al.*, 2010; Milliren *et al.*, 2013). Subcritical conditions could have amplified the effects, as water's higher ionic product facilitated H_3O and OH ion production, which was crucial for autocatalyzing hydrolysis reactions (Kruse & Dinjus, 2007). Acting as a proton acceptor, water's role was further enhanced by the elective extraction of produced glycerol (Ilham & Saka, 2010; Karen dos Santos *et al.*, 2017; Ki *et al.*, 2016). This collective influence potentially could have impacted the release or retention of sulfur compounds, thereby contributing to the observed sulfur content variability. In the autocatalytic process, a free fatty acid dissociates to release a proton. This proton then protonates the carbonyl oxygen of the triacylglycerols (TAG), creating a TAG^+. This protonation allows the carbonyl carbon to undergo a nucleophilic attack by water, thereby promoting the hydrolysis of the TAG. This reaction sequence continues similarly for diacylglycerides (DAG) and monoacylglycerides (MAG) (Minami & Saka, 2006).

$\mathrm{FFA} \rightleftarrows \mathrm{FFA}^- + \mathrm{H}^+$ Dissociation of FFA Equation 4.1

$\mathrm{TAG} + \mathrm{H}^+ \rightleftarrows \mathrm{TAG}^+$ Protonation to TAG Equation 4.2

$\mathrm{TAG}^+ + \mathrm{H_2O} \rightleftarrows \mathrm{DAG} + \mathrm{FFA}^+$ Hydrolysis of TAG Equation 4.3

$\mathrm{FFA}^+ \rightleftarrows \mathrm{FFA} + \mathrm{H}^+$ Deprotonation Equation 4.4

Where: H^+ refers to proton; TAG^+, protonated TAG; and FFA^+, protonated FFA

To sum up, during the hydrolysis process high temperatures and pressures might have altered the properties of sulfur compounds, enhancing their removal. Subcritical water's reduced polarity and dielectric constant at elevated temperatures could have increased the solubility of non-polar organics and facilitated sulfur compound breakdown. These changes, along with improved interactions between water molecules and sulfur compounds, might have enabled more efficient sulfur extraction. This highlights the potential effectiveness of the process in reducing sulfur content in feedstocks. During the first hydrolysis, 95% of the material was recovered from poultry fat and 77% from brown grease, with the second hydrolysis improving recovery to 97% for poultry fat and 96% for brown grease.

4.10.3. Assessing Sulfur Removal Efficiency during Diesel-Equivalent Refining Processes

4.10.3.1. Pyrolysis

During the pyrolysis process, it is plausible to assume that the initial steps of radical degradation might have involved the homolytic cleavage of the S-S bond, which required 74 kcal/mol, and the heterolytic cleavage of the C-S bond, which required 69-75 kcal/mol (Bartoli *et al.*, 2021). This implies that the pyrolysis reaction could have broken the bonds between sulfur atoms or between carbon and sulfur atoms. This could have resulted in the formation of sulfur radicals and promoted the further breakdown of sulfur-containing compounds. The pyrolysis process of free fatty acids from poultry fat resulted in an 87% recovery, while brown grease yielded a 79% recovery of the material.

4.10.3.2. Caustic Washing

The liquid hydrocarbon produced from the pyrolysis process contains organic acids, such as short-chain fatty acids (Beaumont, 1985) and medium-chain fatty acids (Asomaning *et al.*, 2014b). Fatty acids in pyrolysis products pose issues for use in transportation fuels by increasing viscosity and contributing to engine deposits (Knothe, 2009). Furthermore, removing fatty acids during distillation is challenging since some fatty acids' boiling points are too close to those of desired hydrocarbons, necessitating additional purification steps (Omidghane *et al.*, 2020). Therefore, caustic washing of the pyrolysis product was necessary to remove those fatty acids before distillation.

Caustic washing of pyrolyzed products resulted in a 37% and 25% drop in sulfur content for hydrocarbons derived from poultry fat and brown grease, respectively. The significant reduction could be attributed to the breakdown of large sulfur compounds into smaller, more easily removable forms under high-temperature and high-pressure conditions of pyrolysis reactors. This process may have facilitated the removal of sulfur compounds, including those that could have dissolved in basic sodium hydroxide (alkaline) solution during washing. According to Chandra Srivastava, (2012), caustic washing effectively removes low molecular weight thiols. It is possible that this compound was produced during pyrolysis due to the reductive degradation of disulfide compounds (Bartoli *et al.*, 2021). Additionally, caustic washing could have separated hydrocarbons from unconverted free fatty acids by forming sodium soaps, which could trap some sulfur compounds bound to the free fatty acids. This mechanism may have contributed to the lower sulfur content observed in the hydrocarbons after washing. Caustic washing of pyrolyzed hydrocarbons from poultry fat resulted in a 71% recovery, while the same process applied to brown grease achieved an 84% recovery of the material.

4.10.3.3. Distillation

Distillation of pyrolyzed liquid samples further refined the diesel-equivalent products by separating components based on their boiling points. This process allowed for the isolation of the diesel fraction from other pyrolysis byproducts, enhancing the purity and reducing sulfur content in the final product. The distillation process led to a reduction of 16.4% in sulfur content for poultry fat-derived diesel equivalents and 4.2% for those derived from brown grease.

To summarize, the thermochemical conversion of poultry fat and brown grease into diesel-equivalent through hydrolysis, pyrolysis, caustic washing, and distillation significantly reduced the sulfur content by 56 ± 1%, resulting in 43.9 ± 0.6 ppm and 78.4 ± 0.4%, resulting in 111 ± 2 ppm, respectively. The integrated approach enhanced the purity of the final diesel-like products and demonstrated effective sulfur removal. During the distillation of caustic-washed hydrocarbons from poultry fat, 97% of the material was successfully recovered, while the distillation of caustic-washed hydrocarbons from brown grease resulted in a 98% recovery. Therefore, this highlights its potential in sustainable fuel production and environmental remediation efforts.

Hydrolysis Product **Pyrolysis Product** **Caustic washing** **Diesel-Equivalent**

Figure 4.14. General Process Flow for Diesel-Equivalent Production from Poultry fat and Brown grease

4.11. Desulfurization of Produced Diesel-Equivalents using Ultrasonic-Assisted Adsorptive Technique

Previously explored desulfurization techniques proved their ability to remove sulfur compounds from poultry fat and brown grease. After that, the emphasis turned to removing sulfur compounds from diesel equivalents made from these feedstocks. Only ultrasonic-assisted adsorptive desulfurization was employed during this stage since oxidation was considered unsafe for diesel equivalents. Similarly, liquid fuels often use solvent extraction methods to eliminate sulfur compounds from light oil. Nonetheless, sulfur's polarity is slightly different from other aromatic hydrocarbons (Ali *et al.*, 2006). Hence, using only solvent extraction leads to a loss of beneficial hydrocarbons (Abotsi & Scaroni, 1989; Babich & Moulijn, 2003a; Shiraishi *et al.*, 2002).

This study investigated the desulfurization of produced diesel equivalents using the ultrasonic-assisted adsorptive desulfurization method. The initial sulfur content of the poultry fat-derived diesel was 43.9 ± 0.6 ppm. After treatment with various adsorbents, the sulfur contents were reduced to 33 ± 1 ppm with Bentonite, 26 ± 1 ppm with Amberlyst®-A21, 34 ± 1 ppm with Amberlite®-IRC50, and 29 ± 2 ppm with Al-MCM-41. The highest sulfur removal efficiency demonstrated by Amberlyst®-A21 and Al-MCM-41 could be attributed to the strong ion-exchange capabilities of Amberlyst®-A21 and the mesoporous structure of Al-MCM-41, which could have provided a large surface area and suitable interaction with sulfur compounds that facilitated the adsorption. Moreover, Amberlyst®-A21 showed improved removal capability when applied to diesel produced from poultry fat instead of the original poultry fat. This suggested that the sulfur compounds might have undergone changes in their physical or chemical properties, which led them to interact with the surfaces of Amberlyst®-A21. Amberlite®-IRC50 might have less effective functional groups. Conversely, the brown grease-derived diesel had an initial sulfur content of 111 ± 2 ppm. Following treatment with adsorbents, the sulfur levels decreased to 108.8 ± 0.9 ppm with Bentonite, 103 ± 1 ppm with Amberlyst®-A21, 109.9 ±0.7 ppm with Amberlite®-IRC50, 102 ± 1 ppm with Al-MCM-41. The results suggested that the effectiveness of the adsorbents varies significantly for poultry fat and brown grease-derived diesel, likely due to differences in the sulfur compounds present in each feedstock. According to Chandra Srivastava, (2012), diesel contains high-boiling-point organosulfur compounds such as benzothiophenes and dibenzothiophenes, which are difficult to remove due to steric hindrance (Figure 4.15 and 4.16).

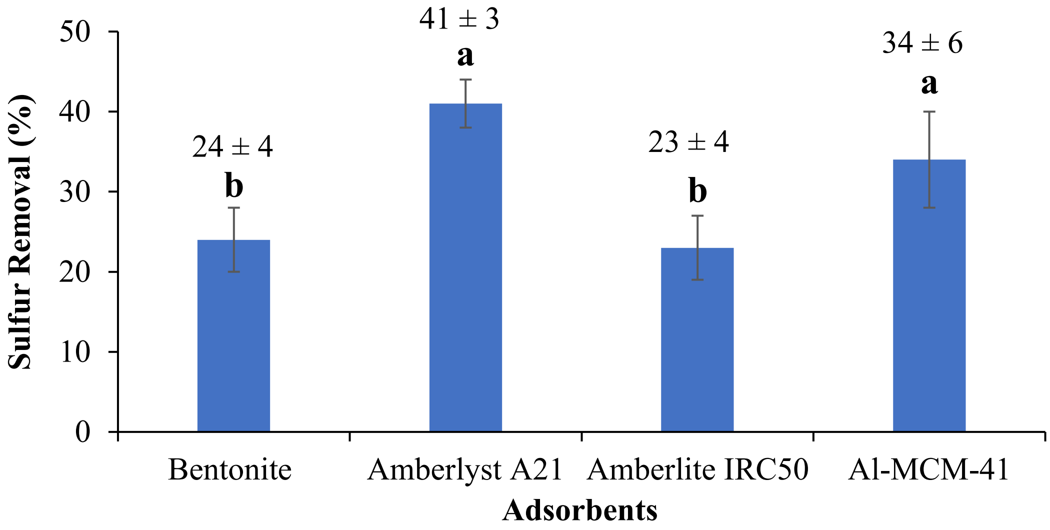


Figure 4.15. Comparison of sulfur removal efficiency of diesel-equivalent produced from poultry fat across various adsorbents through ICP-OES

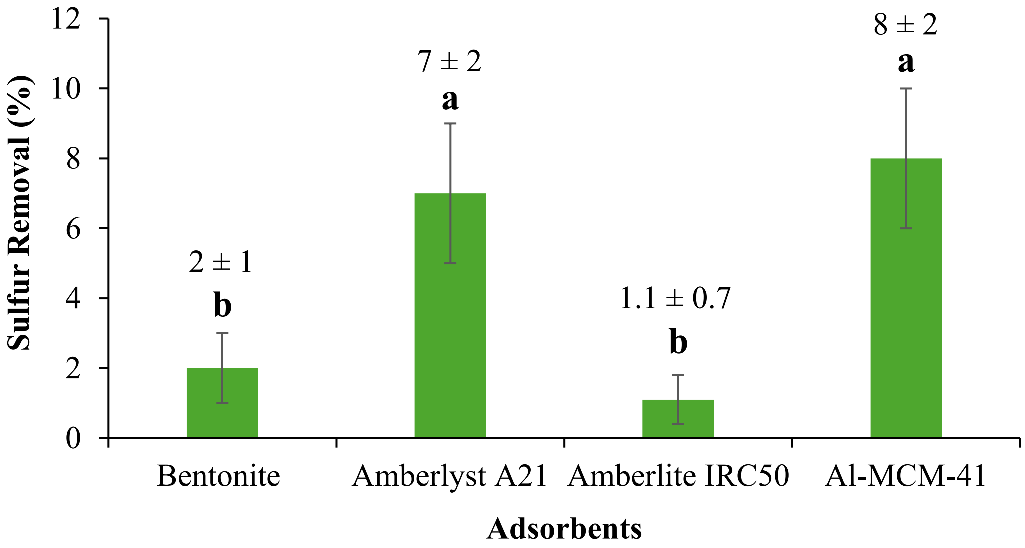


Figure 4.16. Comparison of sulfur removal efficiency of diesel-equivalent produced from brown grease across various adsorbents through ICP-OES

Values are expressed as mean ± standard deviation (n = 3). Different superscript letters (a, b) above bars indicate significant differences between groups at $p < 0.05$. Bars that do not share the same letter are significantly different, the statistical analysis was performed by one-way ANOVA and Tukey's test

According to Lingaiah *et al.* (2005), Bentonite clay is mainly composed of montmorillonite, a cationic clay mineral, while Amberlite®-IRC50 is a cationic resin. This similarity might have enabled both materials to adsorb anionic sulfur compounds, resulting in the observed comparable removal efficiency. Similarly, Mockovčiaková *et al.* (2009) mentioned that the good adsorption capability of bentonite clay comes from its negative charge, which can be neutralized by the adsorption of positively charged anions. Moreover, bentonite is a microporous clay (Azzouz *et al.*, 2006); its surface area might have been limited to adsorb larger molecular-sized sulfur compounds. As mentioned by Shen, (2001), Bentonite has a hydrophilic surface, which could have made it effectively adsorb hydrophilic sulfur compounds due to its affinity for polar substances.

For brown grease-derived diesel, none of the adsorbents tested showed great effectiveness, with Al-MCM-41 and Amberlyst®-A21 showing slightly better performance compared to the rest. Bentonite and Amberlite®-IRC50 were largely ineffective showing < 2% removal. As mentioned in poultry fat-derived diesel, they both exhibit cationic characteristics, which could have led to similar results. Moreover, bentonite is a microporous clay (Azzouz *et al.*, 2006); its surface area might have been limited to adsorb larger molecular-sized sulfur compounds. As mentioned by Shen, (2001), Bentonite's hydrophilic surface could have made it difficult to adsorb hydrophobic sulfur compounds due to its affinity for polar substances. The results shown in Figure 4.12, also highlight the limitations of the current study, as the sulfur compounds in brown grease diesel might be non-polar, have higher molecular weight, or have stronger bonding to the diesel matrix, making them harder to diffuse into the adsorbent pores.

To sum up, ultrasonic-assisted adsorptive desulfurization of produced diesel equivalents demonstrated variable effectiveness, with Amberlyst®-A21 and Al-MCM-41 showing the highest sulfur removal efficiency for poultry fat-derived diesel. However, all tested adsorbents were less effective for brown grease-derived diesel, likely due to the presence of less reactive sulfur compounds like dibenzothiophenes, 4-methyl dibenzothiophenes, and 4,6-dimethyl dibenzothiophenes, which are typically found in diesel fuels (Hernández-Maldonado & Yang, 2004; Mjalli *et al.*, 2014). Their stubborn nature could be attributed to the methyl groups surrounding the sulfur atom, which may create a steric effect (Hernández-Maldonado & Yang, 2004). This underscores the need for further research to develop more effective adsorbents.

5. Conclusions

Desulfurization is a process used to remove sulfur compounds from different types of samples. In this study, various desulfurization techniques such as solvent extraction, oxidation, ultrasonication, and adsorption were applied to remove sulfur compounds from poultry fat (100.0 ± 0.8 ppm), brown grease (515 ± 5 ppm), hardwood (1490 ± 40 ppm) and softwood (2040 ± 40 ppm) crude tall oils. These diverse methods were designed to lower sulfur content and assess each method's effectiveness and suitability for several types of feedstocks. In addition, the thermochemical conversion of these feedstocks into diesel equivalents potentially contributes to renewable fuel production. Lowering sulfur content improves product quality, ensures regulatory compliance, and reduces environmental and health impacts. It also enhances engine and pump performance by preventing corrosion, wear, and deposits in biofuel systems.

The study characterized extracted crude tall oils, confirming the absence of triacylglycerols and the predominance of free fatty acids via thin-layer chromatography. FTIR analysis showed a distinct carbonyl group stretch, indicating soap transformation into free fatty acids. GC-MS-FID analysis revealed higher palmitic and linoleic acids in hardwood oil and more pinolenic and oleic acids in softwood oil. Both types also had substantial amounts of conjugated linoleic acids. In addition, resin acids, terpenoids, and sulfur compounds like dimethyl sulfite and dimethyl disulfide were also identified, indicating a diverse composition of crude tall oils.

The solvent extraction method showed water as the least effective solvent for extracting sulfur from poultry fat, potentially due to its high polarity and poor interaction with the sulfur compounds. Methanol outperformed acetonitrile due to its hydrogen bonding abilities, while diethylene glycol mono ethyl ether was effective, achieving 24 ± 2% sulfur removal, likely due to its amphiphilic nature. However, no significant difference was observed when compared with methanol. Conversely, brown grease dissolved in all the solvents except water, which reduced sulfur content by 50 ± 1%. When washed with the solvents, the sulfur content of hardwood and softwood crude tall oils was significantly reduced by 28-34% and 20-23%, respectively. The findings demonstrate that selecting the appropriate solvent is essential for efficient sulfur removal and feedstock recovery.

This research demonstrated that oxidative desulfurization using H_2O_2 as an oxidant and CH_3COOH as a catalyst in poultry fat and brown grease was significantly influenced by temperature, catalyst-oxidant molar ratio, and catalyst-oxidant concentration relative to feedstock. The highest sulfur removal percentage was achieved at 90 °C, a 1:3.57 molar ratio of acetic acid to hydrogen peroxide, and a 36.5% w/w catalyst-oxidant concentration relative to feedstock. Increased temperatures improved sulfur removal efficiency by speeding up hydrogen peroxide decomposition, enhancing molecular collisions, and reactant diffusion. A higher molar ratio increased proton availability, creating a more acidic environment and enhancing oxidation efficiency. Increasing the concentration of catalyst-oxidant initially enhanced sulfur removal. However, the effectiveness decreased, likely due to reactant limitations, saturation of reactive sites, inefficient breakdown of hydrogen peroxide, and mass transfer issues in complex matrices like brown grease. Therefore, finding the ideal ratios and diffusion dynamics of the catalyst-oxidant concentration relative to feedstock is crucial for maximizing sulfur removal and ensuring effective oxidation in complex samples such as poultry fat and brown grease.

The oxidative desulfurization method effectively transformed sulfur compounds in poultry fat into more polar derivatives, possibly due to the presence of unsaturated fatty acids, with methanol and diethylene glycol mono ethyl ether being the most efficient solvents. Nonetheless, there was no significant improvement in sulfur removal when brown grease was subjected to oxidative desulfurization compared to unoxidized samples. This indicates that the brown grease may have reached a saturation point in oxidation, where further oxidation did not greatly enhance sulfone production. The solidification upon solvent addition made oxidative desulfurization unsuitable for crude tall oils, likely due to the high melting point resin acids present.

Ultrasonic-assisted oxidative desulfurization significantly reduced sulfur levels in poultry fat from 100.0 ± 0.8 ppm to 21.1 ± 0.3 ppm using water as a solvent. Ultrasonication enhanced sulfur compound breakdown, reaction rates, and mass transfer through cavitation effects, proving more effective than previous methods. However, the method demonstrated limited effectiveness in brown grease, possibly due to reaching a saturation point in oxidation or the stable nature of sulfur compounds and the complex composition of brown grease.

In the ultrasonic-assisted adsorptive desulfurization, Al-MCM-41 exhibited superior performance in removing sulfur from poultry fat and brown grease, achieving 38-46% removal. This is possibly due to its large surface area and mesoporous structure. Nevertheless, its fine particulate nature posed separation challenges. Modified bentonites and ion-exchange resins displayed lower efficiency in poultry fat, possibly because of smaller surface areas, less effective pore structures, and limited interactions with sulfur compounds. However, these adsorbents achieved satisfactory sulfur removal of around 40-42% for brown grease. Modification with HCl and iron did not significantly enhance bentonite's performance, and this limited efficiency could be attributed to the nature of sulfur compounds in the feeds and bentonite's hydrophilic surface, which is less effective for adsorbing hydrophobic sulfur compounds. Both anionic and cationic resins showed similar effectiveness, likely due to their ion-exchange capacities and interactions with sulfur compounds. Raw bentonite showed a notable reduction in sulfur levels when used for hardwood (49 ± 3%) and softwood (36 ± 2%) crude tall oils, displaying greater effectiveness in hardwood likely due to variations in sulfur compound characteristics and oil compositions. As the findings highlight, understanding the properties of adsorbents and their interactions with sulfur compounds is crucial for improving desulfurization methods and materials.

Overall, the research successfully reduced the sulfur content in the feedstocks through various desulfurization techniques. For poultry fat and brown grease, the most effective method was ultrasonic-assisted oxidative desulfurization followed by water washing and extractive desulfurization (without oxidation) using water as a solvent, achieving sulfur removal efficiencies of 78.9 ± 0.4% (21.1 ± 0.3 ppm) and 50 ± 1% (257 ± 3 ppm), respectively. For hardwood and softwood crude tall oils, adsorptive desulfurization with raw bentonite clay was the most effective, with removal efficiencies of 49 ± 3% (760 ± 30 ppm) and 36 ± 2% (1300 ± 20 ppm), respectively.

The second approach of the study examined desulfurization during the thermochemical conversion of poultry fat and brown grease. The process involved hydrolysis to break acylglycerols into free fatty acids. Pyrolysis was then applied to convert free fatty acids into hydrocarbons through deoxygenation and thermal cracking.

Subcritical water hydrolysis effectively broke down fats and oils and removed sulfur compounds. This is possibly achieved by utilizing the unique properties of water at high temperatures, such as weakened hydrogen bonds, reduced polarity, and dielectric constant, which may have enhanced the solubility of non-polar organics. These conditions may also alter the properties of sulfur compounds, making their extraction more efficient. This process is autocatalytic, driven by hydronium and hydroxide ions, and the catalytic role of free fatty acids further underscores its potential for industrial applications. Characterization using HPLC-ELSD analysis showed that hydrolysis decreased triacylglycerol content and increased free fatty acids in poultry fat and brown grease, essential for diesel equivalent production. This step had varying effects on sulfur content in poultry fat and brown grease. Poultry fat initially rose in sulfur levels from releasing sulfur-bound compounds but then decreased once glycerol was removed. Conversely, brown grease consistently demonstrated decreased sulfur levels, possibly due to the breaking down of sulfur-containing compounds. This highlights the potential effectiveness of hydrolysis in reducing sulfur content. The pyrolysis process likely broke down large sulfur compounds into smaller, more easily removable forms and removed low molecular weight thiols. Caustic washing of pyrolyzed products reduced sulfur content in poultry fat by 37% and 25% in brown grease. It separated hydrocarbons from unconverted free fatty acids by forming sodium soaps, which could trap some sulfur compounds bound to the free fatty acids. Distillation of caustic-washed samples refined diesel-equivalent products by isolating the diesel fraction, enhancing purity, and reducing sulfur content. This process resulted in a sulfur content reduction of 16.4% for poultry fat-derived diesel and 4.2% for brown grease-derived diesel.

To sum up, turning feeds into diesel-equivalent fuels using hydrolysis, pyrolysis, caustic washing, and distillation significantly lowered sulfur content by 56 ± 1% in poultry fat-derived diesel, yielding 43.9 ± 0.6 ppm sulfur and by 78.4 ± 0.4% in brown grease-derived diesel, yielding 111 ± 2 ppm sulfur. The comprehensive method greatly improved the quality of the final diesel products, showcasing its ability to develop renewable fuel while protecting the environment.

In the third approach, ultrasonic-assisted adsorptive desulfurization successfully decreased sulfur content in poultry fat-derived diesel using Amberlyst®-A21 and Al-MCM-41, reaching levels of 26 ± 1 ppm and 29 ± 2 ppm, with removal efficiencies of 41 ± 3% and 34 ± 6%, respectively. Amberlyst®-A21 worked better on poultry-derived diesel than on poultry fat, indicating possible chemical or physical changes during processing that could have enhanced its interaction with the adsorbent. Conversely, none of the adsorbents were effective on brown grease-derived diesel, likely due to high molecular weight sulfur compounds or their strong bonding to the diesel. This study highlights the challenges of removing persistent sulfur compounds and the need for more effective adsorbents for such products.

In conclusion, the study on desulfurizing low-value agricultural lipid feedstocks and the resulting diesel for renewable fuel applications has yielded promising results that indicated the potential for practical application, emphasizing the importance of selecting the appropriate desulfurization technique depending on the specific feedstock. Based on these results, industries can either remove sulfur at the feedstock or the final product stage by considering different factors such as cost, efficiency, and the specific characteristics of the feedstock. While significant progress was made, meeting stringent regulatory standards of 15 ppm sulfur content remains challenging. Further research is necessary to enhance desulfurization techniques, increase their effectiveness with varying feedstock compositions, and address complicated sulfur compounds. These findings underscore the possibility of producing biorefinery systems that can effectively utilize low-value agricultural lipids to produce renewable fuels while protecting the environment from sulfur emissions.

Recommendations for Future Research

Additional investigations are needed to determine the oxidation reaction's kinetics, order, and rate constant. The impact of pH, adsorbent dosage, and mixed solvents like water-acetonitrile and water-methanol should be examined. Further research should also focus on the effects of oxidative agents and solvents on feeds and diesel equivalents, specifically on properties like density, freezing point, kinematic viscosity, cetane number, and oxidation stability. Moreover, a detailed analysis of the specific sulfur compounds present in both the feedstocks and the diesel produced is suggested to enhance the desulfurization efficiency. Furthermore, techniques should be explored to purify crude tall oils by removing resin acids, and efforts should be made to enhance the recyclability and recoverability of solvents and adsorbents. Lastly, conducting Brunauer-Emmett-Teller (BET) analysis on adsorbents before and after sulfur compound adsorption is recommended to assess changes in surface characteristics like specific surface area and porosity.

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