Purification and Total Acid Number Reduction of Raw Diesel *Via* Column Chromatography.

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Abstract:

Crude petroleum products have impurities that are harmful to industrial equipment, vehicles, and the environment. The American Society of Testing and Materials (ASTM) is a regulatory body that controls the standards for different classes of fuel. These regulations can include acidity, sulfur content, flash point, and many more parameters. ASTM has different standards depending on the type of fuel. For example, diesel that is used in vehicles that are driven on streets is known as road going diesel and has the designated class of ASTM D975. In this research, the standards for ASTM D975 will be used. An unrefined diesel product provided by an industrial collaborator will be upgraded to reach the ASTM standards for acidity and sulfur content. Also, the industrial collaborator asked us to improve the colour and smell of the diesel. Acidity is measured by the total acid number (TAN) with the units of mg of KOH per g of diesel. The TAN value was lowered through acid-base neutralization using different conditions. These conditions include various temperatures, solid KOH, and different concentrations of aqueous KOH solutions with or without a phase transfer catalyst (PTC). A novel technique of using column chromatography was developed to purify the diesel. This technique greatly improved the colour and smell, with colour ranging from an initial brown colour to green or colourless. The odour could be converted to a petroleum like odour from a strong initial camp fire burning aroma. The column was optimized to be run without solvent and the stationary phase recycled. The column can purify up to 800 mL of diesel per 100 g of silica gel and has a recovery of 70%. The TAN value was also reduced to less than 0.03 mg of KOH per gram of diesel using this method of purification.

Acknowledgments:

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List of Abbreviations:

1) Naphthenic Acids (NAs)
2) American Society for Testing Materials (ASTM)
3) Total Acid Number (TAN)
4) Ionic Liquid(s) (IL(s))
5) Supercritical Fluid(s) (SCF(s))
6) Liquid-Liquid Extraction (LLE)
7) Tetrabutylammonium Hydroxide ($[N_{4444}][OH]$)
8) Tetramethylammonium Hydroxide ($[N_{1111}][OH]$)
9) Methyltributylammonium Hydroxide ($[N_{1444}][OH]$)
10) Tetrabutylphosphonium Hydroxide ($[P_{4444}][OH]$)
11) Choline Hydroxide ([Ch][OH])
12) 1-Octyl-3-Methylimidazolium Imidazolide ([OMIm]Im)
13) Supercritical Fluid Extraction (SFE)
14) Supercritical Water (SCW)
15) Water Partial Pressure (WPP)
16) Supercritical Methanol (SC-MeOH)
17) 2,6-Naphthalenedicarboxylic Acid (NDAC)
18) Methanol Partial Pressures (MPP)
19) Hydrodesulfurization (HDS)
20) Hydrogen Disulfide (H_2S)
21) Ultra-low Sulfur Petroleum (ULSP)
22) Dibenzothiophene (DBT)
23) 1-Alkyl-3-Methylimidazolium Bistriflamide ([Cnmim] [NTF2])
24) Rhodococcus Erythropolis (R. XP)
25) Tetrahydrofuran (THF)
26) Tetramethylammonium Chloride ($[N_{1111}][Cl]$)
27) Tetraethylammonium Chloride ($[N_{2222}][Cl]$)
28) Tetrabutylammonium Chloride ($[N_{4444}][Cl]$)

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1. Introduction:

1.1 Background:

In 2001, roughly 735 000 barrels of heavy crude oil was extracted from the Alberta oil sands.[1] With all the bitumen being extracted, it must be processed into its usable components for consumption. This process involves production, transportation, and efficiently refining the bitumen/oil so it is inexpensive. Problems with processing oils are presented by metals, sulfur and nitrogen containing compounds, and naphthenic acid (NA) contaminants.[2] The removal of contaminants is important in the refining process, because these compounds can cause problems like destroying expensive equipment and adversely affecting the environment. To help combat these issues, regulatory bodies such as the American Society for Testing Materials (ASTM) help determine the standards that companies must follow with regard to delivering their fuels to consumers. ASTM standards include flash point, acidity, sulfur content, viscosity, and many more factors/values. In this research project the focus will be on the acidity and the sulfur content found in fuel. ASTM is broken down into classes that apply to different types of fuel. These classes can be, for example, road going diesel that can be accessed from a gas station; another would be diesel used in industrial vehicles, which have different standards associated with them. The standard that will be used in this current research is that of ATSM D975, where D975 is the class for road going diesel. Only two values will be important from this standard, which are for acidity and sulfur content. The molecules that cause acidity and high sulfur will be explored and how they affect the industrial process and their effect on the environment.

1.2 Naphthenic Acids (NAs):

NAs are mixtures of cyclic aliphatic, and linear monocarboxylic acids found in petroleum, oil sands bitumen, and crude oils deposits,[3] with the formula $C_nH_{2n+z}O_2$, where n is the number of carbons and z indicates the deficiency of hydrogen, which is given as zero or a negative even integer.[4] NAs come from aerobic microbial degradation of hydrocarbons and from the break-down of plant and animal matter.[5] NAs are known to be chemically stable, non-volatile, and act as good surfactants. With an increase in molecular weight, NAs become more polar and non-volatile, changing their physical and chemical properties.[6] NAs are carboxylic acids, which are the source of acidity in petroleum fuels and other similar products, with pKa's comparable to large fatty acids but not as strong compared to acetic acid. The pKa of NAs in crude oil was found to be 4.9.[7] NAs do have other uses in industry as timber antiseptics and paint drying reagents.[8] The main problem that NAs present in industry is that they are dangerous for pipelines and refineries as the acidity can corrode these pieces of equipment.[9] The corrosion of the steel alloys in pipes is believed to be due to NAs chelating to the metal surface through the carboxylic acid, and slowly eroding it.[10] According to ASTM, acidity is measured using the total acid number (TAN), which is the milligrams of potassium hydroxide required to neutralize 1 gram of petroleum product. For the ASTM standard D975, the TAN value needs to be below 0.5 mg of KOH per 1 g of fuel and a TAN higher than 0.5 mg of KOH/g is considered highly acidic and corrosive.[11] Even though the main issue with NAs is that they are highly corrosive, they can have a harmful effect on the environment as well. A study done by Holowenko found that waste water from refining plants in Alberta had enough NAs to pollute nearby ponds, with increasing levels of NAs of 20-120 mg/L, where 2.5-5 mg/L is toxic to fish life.[12]

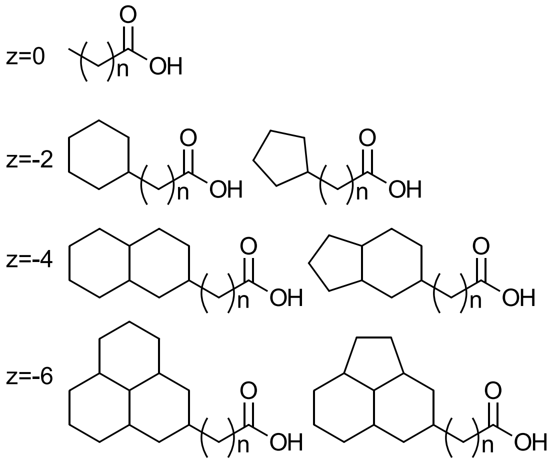

Figure 1: Different types of NAs

1.3 Method for TAN Value Reduction:

Methods to reduce the TAN commonly include solvent extraction, decarboxylation, and esterification.[13] A very crude way of lowering TAN values that is used in industry is to mix high TAN oil with low TAN oil to bring the average below the 0.5 mg of KOH/1 g standard. The issue is that crude oil is never found with low amounts of NAs, necessitating the lowering of acidity. Also, the mixing of the oils does not remove NAs therefore the same total amount is present.[14] Solvent extraction can be broken down into three main components.[2] There are ionic liquids (ILs), super critical fluids (SFC), and aqueous acid/base extractions. The main premise of extraction of NAs from oil products is to use solvents for liquid-liquid extraction (LLE) or to convert the NAs to a more soluble form for the solvent to extract. Basic aqueous washes are a common industrial method in the removal of NAs, using bases like $Ca(OH)_2$ and NaOH to convert the NAs to their sodium/calcium naphthenate derivatives, which are more soluble in the aqueous phase. Acid then can be added to recover the NAs for uses in other parts of industry.[15] The issue with this method is that NAs will cause the formation of emulsions and have low solubility in the aqueous phase. The use of organic bases with ethanol has been attempted in extraction, however stronger organic bases are required, and the base can be left over in the oil.[16]

1.4 Aqueous Extractions:

What can also be used in aqueous extraction is a phase transfer salt that aids in the transfer of hydroxide ions from the aqueous phase into the oil phase, where the hydroxide ion reacts forming the naphthenate ion that is transferred by the phase transfer salt into the aqueous phase. Syed Nasir Shah used ammonium hydroxide salts to aid in the transfer of hydroxide ions into the oil phase.[17] The salts that Shah attempted to reduce the TAN value with were tetrabutylammoniumhydroxide ($[N_{4444}][OH]$), tetramethylammoniumhydroxide ($[N_{1111}][OH]$), methyltributylammoniumhydroxide ($[N_{1444}][OH]$), tetrabutylphosphoniumhydroxide ($[P_{4444}][OH]$), and choline hydroxide ([Ch][OH]). Shah and co-workers can remove 100 % of the NAs with $[N_{1111}][OH]$ up to a TAN value of 5 mg of KOH/1 g before any loss in percent removal. Shah also showed that these salts can be reused up to five times for extraction before performance decreases. Shah used one equivalent of salt to remove the NAs, but this can be converted to a catalytic cycle by adding a hydroxide base. The hydroxide can do an ion exchange with the naphthenate ion, regenerating the phase transfer salt to extract again; this is known as phase transfer catalysis. See Figure 2 for the catalytic cycle. Similar to normal aqueous extraction, the oil will still form emulsions and have slow extraction rates.

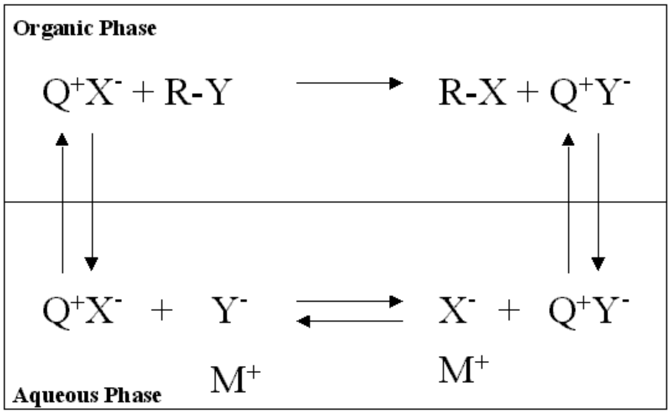

Figure 2: Phase transfer catalyst cycle

1.5 Ionic Liquid Extractions:

ILs are ionic salt materials that have a low melting point that is usually below 100 °C. ILs have a charged cation that is a large bulk organic structure and an anion that is held together with Coulombic interactions. With these ionic bonds, ILs are non-volatile and non-flammable.[18] The cation can be a base of ammonium, sulfonium, phosphonium, imidazolium, pyridinium, pyrrolidinium, and many more, which can be derivatized. The anions can be halides, which are known as first generation ILs. The anions can also be organic ions like acetate or benzoate, or the anion can be inorganic, such as $[BF_4]^-$, $[PF_6]^-$ and many more. By varying the cation and anion, the physical properties of ILs can be tuned for optimal use.[19] ILs can be used as solvents and catalysts in reactions, being a greener alterative compared to organic solvents and heavy metal catalysts. What has been developed in recent years is the use of ILs in the extraction of NAs from crude oil and similar products. ILs also do not form emulsions with NAs in oil, adding additional benefits for using ILs over aqueous extraction. Sun and Shi were able to demonstrate that ILs can be used to extract NAs using imidazolium imidazolide derivatives.[21] Out of Sun and Shi's IL derivatives, it was determined that 1-octyl-3-methylimidazolium imidazolide ([OMIm]Im) gave the best performance at 100 % removal after 2 hours at 50 °C and that the IL was able to be reused 8 times before loss of activity.[20] Sun and Shi also studied derivatives of bipyridine, pyridine, and imidazole ILs, but the ([OMIm]Im) IL still gave the best performance.[21] Shah has also done IL extractions using imidazole as the cation with changing the side chain from a length of 4 carbons long to 12 carbon derivatives. The anion of choice for Shah was the phenoxide ion. Shah was able to obtain an extraction time needed for 100% removal of NAs of 1 hour at 30 °C with the 12 carbon derivative.[22] Ionic liquids are relatively new in the scene of NA extractions and more research needs to be conducted before it can be a viable industry process, and Shah states this himself in his paper as the prices of ILs must decrease and reusability needs to be more efficient before widespread adoption.

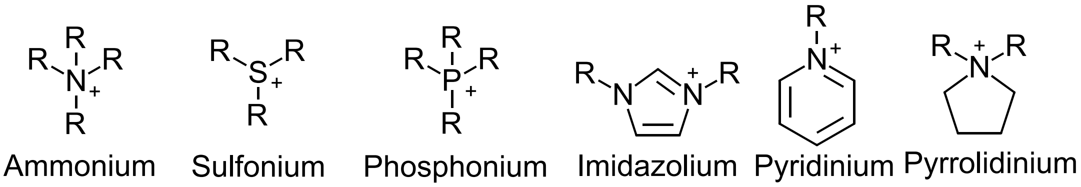

Figure 3: Common structures of cation for ILs.

1.6 Supercritical Fluid and Esterification:

A super critical fluid (SCF) is when the temperature and pressure of a substance is raised above its critical point, where a difference between liquid and gas phases no longer exists. Common SCFs are prepared with carbon monoxide, methanol, water, acetone and many more. SCFs can act as solvents in reactions and are often considered as green solvents. SCFs are used for supercritical fluid extraction (SFE) in the decaffeination of green coffee, and the production of food, nutraceuticals, perfumes and cosmetics, pharmaceuticals, textiles, electronics, aerogels, ceramic and innovative materials, oil industry, laundry dry cleaning, generation of co-crystals in pharmaceutical processes, and biodiesel production.[23] SCFs can either extract the NAs from the oil or react with the NAs to remove the carboxylic acid functionality. When performing SFE, supercritical water (SCW) is used as a solvent for its ability to extract NAs from the oil. SCW can also promote oxidation and hydrolysis at higher temperatures, breaking down heavy crude oil like tar to more usable materials.[24,25] A study by Mandala used SCW to extract NAs from crude oil, by changing temperature, extraction time, and water partial pressure (WPP). Mandala optimized extraction conditions, which resulted in an 83 % removal of NAs at 490 ^oC with a WPP of 45 MPa for 90 mins.; the WPP had little effect on the percent removal.[26]

What also can be done with SCFs is the use of supercritical alcohols (like supercritical methanol SC-MeOH) to form esters. This leads to other methods of lowering the TAN value by chemically changing the carboxylic acid group of the NAs. There are two major methods of chemical transformations of NAs: esterification and decarboxylation. Esterification converts the carboxylic acids into esters, usually methyl esters as methanol is a cost-effective reagent to use. The major benefit of esterification is that the total mass is not reduced after the TAN reduction as the NAs were not removed from the oil itself. Protic acids cannot be used as this would cause the addition of acid to the oil, increasing the TAN value. Instead, Lewis acids like Al_2O_3 and SnO_2 are preferred as they are inexpensive, good catalysts, and easily removable.[27] SC-MeOH can also be used to perform esterification as the elevated temperature aids in the reaction rate and using SC-MeOH as solvent helps drive the reaction towards the ester. Another study was done by Mandala using SC-MeOH to convert 2,6-naphthalenedicarboxylic acid (NDAC) into its ester derivative. At a temperature of 220 ^oC with methanol partial pressures (MPP) of 0.1 MPa for 60 mins only 52.12% of NDAC was converted to the ester.[28] Faisal Zafar also used SC-MeOH with 1-butyl-3-methylimidazolium octylsulfate as an IL catalyst in esterification. Zafar was only able to convert 55% of NAs into esters.[29]

1.7: Decarboxylation and Other Methods:

Decarboxylation is the process in which a carboxylic acid is cleaved off as a CO_2 molecule. This reaction can be used in lowering the TAN value by removing the acidic functionality of the NAs entirely. This method also results in less loss of mass compared to extraction methods, as CO_2 is substantially smaller compared to the mass of a NA, and CO_2 can be collected to be used in other processes.[30] A study done by Aihua Zhang compared the differences between metal oxides of the alkaline earth metals starting from magnesium.[30] At 250 ^oC, it was found that calcium oxide was able to decarboxylate the NAs with a conversion above 90%, where magnesium oxide was only able to reach a conversion of 80%. The only metal reaction from which Zhang was able to collect CO_2 was magnesium. With some optimization, the decarboxylation with magnesium can convert 95% of NAs with a catalyst loading of 40% and collect about 20% of the total expected CO_2 at 250 ^oC. Magnesium is an inexpensive metal that at a high catalyst loading does not have a significant cost impact compared to noble earth metals. Xiaoqin Fu has done work using different catalysts of Al_2O_3 and quartz sand. Fu found that Al_2O_3 outperforms quartz sand. The downside of this is that to obtain 100% conversion, the temperature required for Al_2O_3 needs to be 480 ^oC.[31] Another study done by Heloísa P. Dias used steel slag as a catalyst at 350 ^oC and only obtained a reduction of the TAN value of 43%.[32] Research done by Lianhui Ding discovered that CaO and BaO with particle size of 300 Å converted all NAs at 300 ^oC.[33] Supported palladium and platinum can also be used in decarboxylation of NAs. These supported catalysts can decarboxylate a variety of fatty acids at temperatures between 80–100 °C without the need for any hydrogen.[34] Titanium-based catalysts can decarboxylate NAs as well and are resistant to poisoning from sulfur molecules.[35] Catalytic reactions that involve palladium and platinum can be killed with the presence of sulfur molecules, as the sulfur will readily coordinate to and poison the catalyst.[36] This can be a problem as sulfur can be found in crude oil and will have to be removed before the use of this method. The issues with using palladium and platinum as catalysts are the high costs for these rare noble metals.

Other methods can consist of metal oxide adsorption using magnesium and aluminum oxides. These metal oxides show high adsorption for NAs of 95% at temperatures of 30-80 ^oC.[15] The metal oxide can be reused as the NAs can be easily removed. Disadvantages of this method are that it only works on low boiling fractions of oil and needs stronger bases such as NaOH, $Ca(OH)_2$, etc. The base is constantly neutralized by the acidic NAs of the oil and needs to be replenished often, costing money and resources.[37] It also does not help that the used waste water is toxic to the environment.

1.8 Removing Sulfur:

Sulfur is an important element to remove from crude oil and petroleum products. The sulfur can be dangerous to the refinery as it can bind to metal surfaces and corrode the equipment. Sulfur can also poison metal-based catalysts used in the fuel refinery, increasing the cost for replacement. Also, sulfur found in fuels that are used on the roads will burn and produce harmful SO_x molecules. These SO_x molecules are known to be greenhouse gases and SO_4^{2-} is the main cause of acid rain.[38] Without controlling the total amount of SO_x molecules being placed into the environment, the impact of these gases can damage ecosystems and infrastructure. The type of molecules of sulfur that can be found in oil consist of thiols, sulfides, disulfides, and thiophenes and make up about 2% of crude oil extracted. ASTM has a very low limit of 15 ppm of sulfur that can be found in diesel.

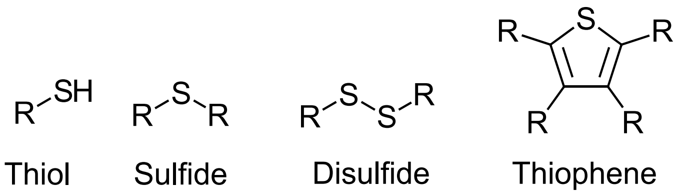

Figure 4: General structure of common sulfur molecules in oil.

When it comes to removing sulfur in industry, there is only one method that is commonly used: hydrodesulfurization (HDS). HDS is a physicochemical process that catalytically breaks apart organo-sulfur molecules by preheating the oils and mixing with hot recycled gas containing hydrogen. This mixture is then reacted with the HDS catalyst in a bed reactor, known as the hydrotreater, at temperatures between 290-445 °C and pressures between 150-3000 psi, which then converts the organosulfur compounds to non-sulfur organics and hydrogen disulfide (H_2S) gas.[38] The HDS catalysts are commonly made of molybdenum sulfide that is doped with other metals such as cobalt and nickel. HDS has challenges with reaching ultra-low sulfur petroleum (ULSP). It is an energy intensive process and HDS has problems removing some sulfur compounds, in particular dibenzothiophene (DBT), leading to the need for higher temperatures, more energy, and larger reactors. Recent methods being developed in sulfur removal include ILs, bio-desulfurization, and heterogeneous photocatalytic desulfurization.

Similar to using ILs in removing NAs from petroleum, the use of ILs to extract sulfur uses the same premise of solubility: the sulfur molecules are more soluble in the IL phase compared to petroleum. This also includes DBT molecules that HDS has a difficult time reducing. ILs can be coupled with HDS to make ULSP by lowering the sulfur and removing DBT to a level where HDS can remove the rest.[39] While the use of ILs for extraction of sulfur has been reported to be feasible on a laboratory scale, a simulation was performed by Paul Nancarrow to evaluate efficacy at an industrial scale.[38] The simulation examined 1-alkyl-3-methylimidazolium bistriflamide ([Cnmim] [NTF2]) as the IL. It was determined that IL extraction in combination with HDS to achieve ULSP specifications is possible and benign and presents an alternative to the use of HDS only. HDS can be the first treatment, followed by IL extraction to bring the sulfur content from 50 ppm to 10 ppm. It was concluded that due to the IL prices, the ILs desulfurization technology is not yet economically feasible. With a potential drop in IL prices, IL extraction can soon become more popular than HDS.

Heterogeneous photocatalytic desulfurization has a strong chance to surpass HDS because of high sulfur removal efficiency and low operational costs. This method uses nanoparticles of cadmium oxides under visible-light irradiation to create electron-hole pairs, which then form free radicals that perform photo-oxidation of sulfur molecules and convert them into sulfoxides and sulfones. This method performed by Asmaa S. Morshedy yielded a desulfurization capacity of 99.6% from 11,500 ppm to 45 ppm.[8] As cadmium is a highly toxic element, its removal from fuel is critical, as any lingering cadmium can have adverse effects on the environment and the consumer.

An interesting development in sulfur removal is the use of biological catalysts that are used in the break-down of sulfur molecules. These bio-catalysts are made up of strains of an aerobic soil-isolated bacteria, *Rhodococcus erythropolis* (R. XP).[40] R. XP was determined to efficiently desulfurize DBT and it has been reported that the bacterial catalyst can reduce the sulfur content of oil from 259 to 14 ppm, a decrease of 94.5% in 24 h at 30 °C.[41] The main issue of biodesulfurization is an inability to perform it on an industrial scale, which considers the requirements for separation, oxygen content, product recovery, and recycling of the biocatalyst . Other such biocatalysts for removing sulfur compounds include the use of hemoproteins to bio-oxidize organosulfides and thiophenes to form sulfoxides and sulfones. One specific method makes use of *Caldariomyces fumago*, which is a chloroperoxidase microorganism, which halogenates organic molecules with the use of hydrogen peroxide. In the presence of hydrogen peroxide and sulfur molecules, *Caldariomyces fumago* decreased the sulfur content in diesel fuel by 83%.[42] The biocatalyst can function in a wide range of pH (between 2-11), has broad specificity, and is relatively inexpensive. The use of halogens in this method can cause some environmental problems and for this method to be viable in industry, this enzyme needs to function in low-water content conditions.

1.9 Research:

In this project, research will be conducted on a raw diesel sample that was supplied by an industrial collaborator to reach the standards given by ASTM D975. The company's diesel does not meet the requirements for the standards in the sulfur content and acidity. The main goal of this research is to bring the TAN and sulfur values down to below the required limits. We were also asked to improve the odour and colour of the diesel. Column chromatography will be used to aid in improving the colour, smell, and lowing the sulfur content. Bases will be added to the diesel in an attempt to lower the TAN value, with different conditions being applied to find the optimal conditions.

2. Experimental:

2.1 Materials:

All solvents used were obtained from Fisher Chemicals. Silica gel that was used was a mesh size of 120-200 and was obtained from Silicycle Inc.. Activity I alumina had a mesh size of 70-230 and was obtained from Merck. KOH, Celite, charcoal, and $MgSO_4$ were obtained from ACP chemicals. $[N_{1111}][Cl]$, $[N_{2222}][Cl]$ and $[N_{4444}][Cl]$ were obtained from Sigma-Aldrich.

2.2 General Information:

The vacuum pump used was a Welch Duoseal vacuum pump 1399 series and was determined to function at 10 mTorr. The vacuum pressure was determined using a McCloud gage. Oven drying was done at 75 ^{o}C for reactivation of silica gel. The terms raw, green, and clear diesel are terms used to describe diesel herein. Raw diesel is the initial starting diesel. Green diesel is a partially purified diesel that is green in colour, and clear diesel is a highly-purified diesel that is colourless. The term for dark and light silica comes from recycled silica gel. Dark silica gel is from silica gel that has been cleaned with methanol to remove brown impurities and is dark in colour. Light silica gel is silica gel cleaned with ethyl acetate and is the lightest out of the recycled silica gels.

2.3 Methods:

Column chromatography will be used in an attempt to remove sulfur from the raw diesel, as the more polar organosulfur molecules will be retained by the stationary phase of the column.[43] The stationary phase will be optimized along with the solvent. Stationary phases such as silica gel and alumina will be tested with solvents of chloroform, ethyl acetate, diethyl ether, tetrahydrofuran (THF), pentane, and hexanes. All columns for optimization will be performed on small scale of 25 mL and large scale of about 500 mL. Our industrial collaborator will contract an external company to determine the sulfur content. Improvements to the colour and smell will be determined qualitatively.

In TAN reduction tests, diesel that was first cleaned using column chromatography will be used and three different inorganic bases consisting of KOH, K_2CO_3, and $NaHCO_3$ will be used to determine the optimal base for neutralization. The optimal conditions for reduction will be explored, which consist of addition of solid KOH, KOH as aqueous solution, and aqueous solutions of KOH with a 0.1% wt/v PTC. Also increased temperature will be used to observe the effect on TAN reduction.

To determine the TAN value of the diesel, instead of performing a titration using pH, conductivity will be used. Conductivity is known to get faster and more accurate results than using pH.[44] Dr. Young helped set up the titrator that was used in determining the TAN value.[44] The most important part of the set-up is to have the burette plugged with a small hole with a tube that runs close to the bottom under the titrant. This allows the drops to fall at a constant rate. To control the drop rate, two stock cocks are needed: one to control the rate of drops and the other is an open and close valve (see Figure 5). Data was collected using a Vernier Software and Technology conductivity probe with Logger Pro 3.10.1 software. To calculate the equivalence point of the titration, as seen in figure 6 there is a change of slope in the graph; the intersection of these slopes is called the inflection point. Using the inflection point, the TAN value can be calculated using equation 1. Alcoholic KOH solutions were prepared every day and the molarity was determined using equation 2.

$$\text{TAN} = \frac{\left(\frac{\text{Initial mass of titrant} - \text{Final mass of titrant}}{\text{Density of solution}}\right) \text{x} \left(\frac{\text{Inflection time}}{\text{Total time}}\right) \text{x(Molarity of KOH)x(Molecular weight of KOH)}}{\text{Mass of diesel used}}$$

Equation 1: TAN value

$$\text{Molarity of KOH} = \frac{\text{Moles of HCl}}{\left(\frac{\text{Initial mass of titrant} - \text{Final mass of titrant}}{\text{Density of KOH solution}}\right) \text{x} \left(\frac{\text{Inflection time}}{\text{Total time}}\right)}$$

Equation 2: Molarity of alcoholic KOH

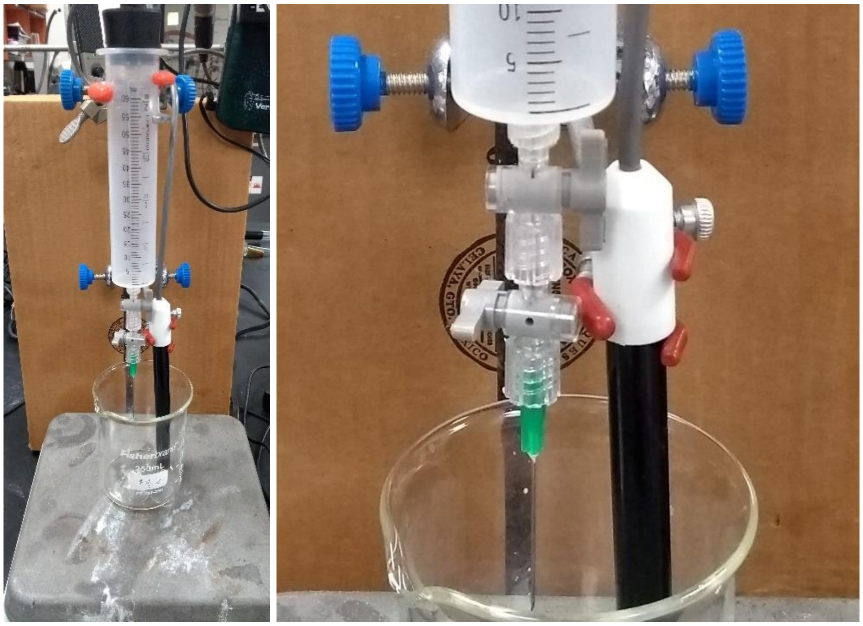

Figure 5: Titration and Stopcock set up**.**

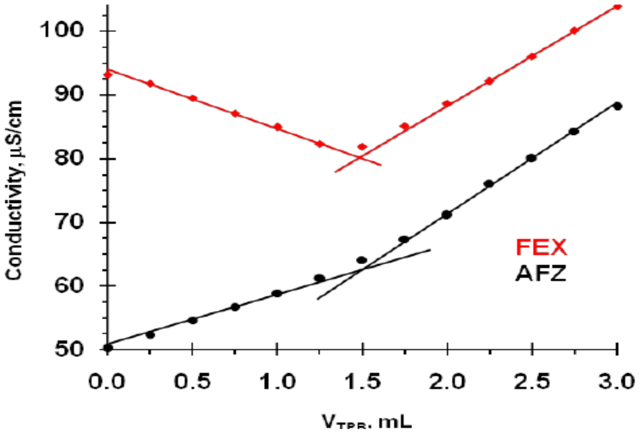

Figure 6: Titration graph with conductivity, red is strong acid with strong base and black is a weak acid or base with a strong acid or base.

Charcoal and Diesel:

10 g of raw diesel was stirred for 2 hours with 5 g of charcoal. The mixture was then filtered *via* gravity filtration. Chloroform was needed to help the diesel to filter properly, as the diesel would not flow through the filter paper easily. The colour of diesel after the solvent was removed on the rotary evaporator remained the same.

Diesel and Celite:

A celite bed was prepared by suspending celite in chloroform and packing a bed that is 3 cm thick. 10 g of raw diesel diluted in 10 mL of chloroform, mixed with charcoal was then passed through the celite bed and solvent removed on the rotary evaporator

2.4 Column Optimization:

Column V.1.0: Silica Gel and Chloroform

A column 2.54 cm in diameter was wet packed with 15 cm of silica gel in chloroform. 25 mL of raw diesel was then added to the column and passed through by topping up the column with chloroform. Two different coloured fractions separated; the first to elute from the column was yellow in colour. Once all the solvent was removed, the colour of the first fraction was a dark orange. The other fraction was a brown colour that eluted from the column with the aid of ethyl acetate. Removing the solvent resulted in a thick brown liquid.

Column V.1.1: Alumina and Chloroform

A column 2.54 cm in diameter was wet packed with 15 cm of activity I alumina in chloroform. 25 mL of raw diesel was placed on top of the column and passed through with chloroform. Two coloured fractions separated. The first to elute from the column was yellow in colour. The second fraction needed ethyl acetate to elute from the column; this fraction was brown in colour. After all the solvent was removed, the first fraction resulted in a yellow colour, and second was a dark brown.

Column V.1.2: Alumina and THF

A column 2.54 cm in diameter was wet packed with 15 cm of activity I alumina and THF. 25 mL of raw diesel was placed on top of the column and passed through with THF. Similar to chloroform, two colour fractions separated. The first to elute from the column was yellow in colour. The second fraction needed ethyl acetate to elute from the column, which was brown in colour. The first fraction resulted in a yellow colour, and the second was a dark brown once all the solvent was removed using the rotary evaporator.

Column V.1.3: Alumina and Diethyl ether

A column 2.54 cm in diameter was wet packed with 15 cm of activity I alumina and diethyl ether. 25 mL of raw diesel was placed on top of the column and passed through with diethyl ether. Same as THF and chloroform, two colour fractions separated. The first to elute from the column was yellow in colour. The second fraction needed ethyl acetate to elute from the column and was brown in colour. The first fraction resulted in a yellow colour, and the second was a dark brown once all the solvent was removed.

Column V.1.4: Alumina and Hexanes

A column 2.54 cm in diameter was wet packed with 15 cm of activity I alumina and hexanes. 25 mL of raw diesel was placed on top of the column and passed through with hexanes. The diesel separated into three fractions. The first fraction was green in colour, followed by the second which was a yellow colour. The third faction was a brown colour and needed ethyl acetate for separation. After all solvent was removed, the first fraction was green, the second fraction was yellow, and the third fraction was a dark brown colour.

Column V.1.5: Alumina and Pentane

A column 2.54 cm in diameter was wet packed with 15 cm of activity I alumina and pentane. 25 mL of raw diesel was placed on top of the column and pentane was passed through the column. There was not any separation and the raw diesel did not move through the column. The solvent was changed over to hexanes to elute the diesel through the column.

Column V.1.6: Silica Gel and Hexanes

A column 2.54 cm in diameter was wet packed with 15 cm of silica gel and hexanes. 25 mL of raw diesel was placed on top of the column and passed through with hexanes. The diesel separated into three fractions: the first was green in colour, followed by the second which was yellow in colour, and the third fraction was a brown colour and needed ethyl acetate to elute from the column. After all the solvent was removed, the first fraction was green, the second fraction was yellow, and the third fraction was a dark brown colour.

2.5 Large Scale Column:

Column V.2.0: 5.08 cm Diameter Column Filled with 30 cm of Silica with 200 mL of Raw Diesel

A column 5.08 cm in diameter was wet packed with 30 cm of silica gel and hexanes. 200 mL of raw diesel was placed on top of the column and passed through with hexanes. The same separation seen in V.1.6 was observed. After the solvent was removed, the total amount of green colour diesel collected was 130 mL out of the 200 mL separated with a % recovery of 65%.

Column V.2.1: 7.62 cm Diameter Column Filled with 450 g of Silica with 500 mL of Raw Diesel

A column 7.62 cm in diameter was wet packed with 450 g of silica gel and hexanes. 500 mL of raw diesel was placed on top of the column and passed through using hexanes. The green diesel was collected, and the solvent was removed using the rotary evaporator, and the sample was placed under a vacuum over night to remove all the solvent. 350 mL of green diesel was collected out of the 500 mL of raw diesel used, a percent recovery of 70 %.

Column V.2.2: Column V.2.1 with Vacuum

A column 7.62 cm in diameter was wet packed with 450 g of silica gel and hexanes. 500 mL of raw diesel was placed on top of the column and passed through using hexanes. The end of the column was attached to a tube running to an aspirator vacuum with a trap flask in between. The top of the column was connected to a tube running down into a solvent reservoir, see Figure 7. Light vacuum was applied at the end of the column draining the solvent from the column and collecting the eluent into the trap. Also, the solvent was then dragged up the tube into the column constantly refilling itself. About 350 mL of green diesel was collected with a percent recovery of 70%.

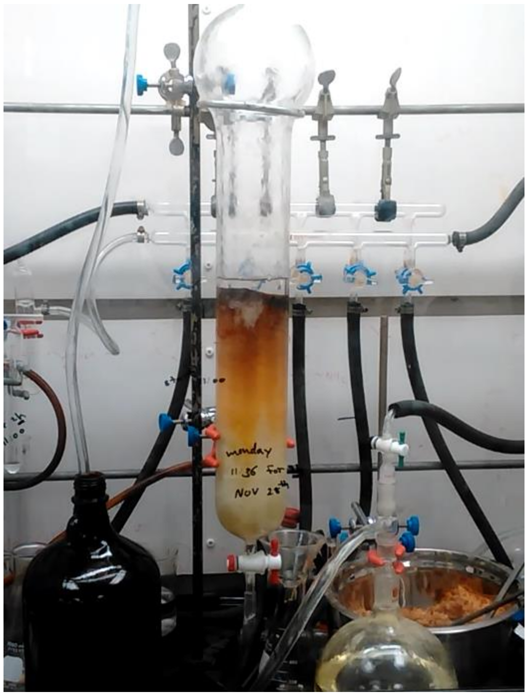

Figure 7: Column V.2.2 with vacuum attached to pull solvent into column.

Column V.2.3: Column V.2.2 Without Solvent

A column 7.62 cm in diameter was packed with 450 g of silica gel. 500 mL of raw diesel was placed on top of the column and using the vacuum step up in column V.2.2, light vacuum was applied. Once all 500 mL of the diesel had eluted into the column the movement of the diesel through the column stopped. The vacuum was changed from the aspirator vacuum to the Schlenk line pump. The stronger vacuum started to elute the diesel from the column. Without solvent a new fraction can be seen. This fraction elutes off the column first and is clear in colour. The rest of the fractions are the same as found in column V.1.6.

Column V.2.4: 7.62 cm Diameter Column Filled with 150 g of Silica with 500 mL of Raw Diesel

A column 7.62 cm in diameter was packed with 150 g of silica gel. 500 mL of raw diesel was placed on top of the column and using the Schlenk line vacuum was eluted through. About 300 mL of the 500 mL raw diesel was collected in the form of the clear colour diesel previously shown to be separable in column V.2.3. Another 150 mL of the green/yellow diesel was collected. A column 7.62 cm in diameter was packed with 150 g of silica gel and 300 mL of the green/yellow diesel collected was passed through using the Schlenk line vacuum. About 175 mL of clear diesel separated and the rest was green/yellow in colour.

Column V.2.5: 2 Tandem Columns

Two columns 5.08 cm in diameter where prepared and attached via a tube, seen in Figure 8. The first column was packed with about 10 cm of dark silica gel and the second column was packed with 20 cm of light silica gel. Dark and light silica gel are the two versions of reused silica gel, see below. 500 mL of diesel was placed onto the first column and with the Schlenk line vacuum was eluted through the first column and transferred to the second, where clear diesel is then collected in the trap flask. About 350 mL of the clear diesel collects before any green/yellow colour begins to elute.

Figure 8: Column V.2.5 setup.

Column V.2.6: Capacity of Fresh Silica Gel

A column 5.08 cm in diameter was packed with 100 g of silica gel. 500 mL of raw diesel was placed on top of the column and with the Schlenk line vacuum the diesel was loaded onto the column. Once all the diesel loads onto the column, 50 mL of raw diesel was used to top up the column. This was repeated until the eluent from the column became brown in colour. This amount of diesel placed into the column will be considered its capacity.

Column V.2.7: Capacity of light Silica Gel

A column 5.08 cm in diameter was packed with 100 g of light silica gel. 500 mL of raw diesel was placed on top of the column and with the Schlenk line vacuum the diesel was loaded onto the column. Once all the diesel loads onto the column, 50 mL of raw diesel was used to top up the column. This was repeated until the eluent from the column became brown in colour. This amount of diesel placed into the column will be considered its capacity.

Column V.2.8: Capacity of Dark Silica Gel

A column 5.08 cm in diameter was packed with 100 g of dark silica gel. 500 mL of raw diesel was placed on top of the column and with the Schlenk line vacuum the diesel was loaded onto the column. Once all the diesel loads onto the column, 50 mL of raw diesel was used to top up the column. This was repeated until the eluent from the column became brown in colour. This amount of diesel placed into the column will be considered its capacity

2.6 Reusability:

Solvents:

For the large-scale columns V.2.2 and V.2.3, about 4 L of hexanes solvent is used. Solvents were recollected to save on cost. Solvents that were recycled were hexanes, ethyl acetate, and methanol. The majority of the solvents were recollected from the rotary evaporator. Solvents that could not be collected from the rotary evaporator, were collected by distillation under vacuum using a liquid nitrogen trap.

Silica Gel:

Depending on what has been passed through the silica gel, the solvent used to clean the gel will change. If the raw diesel was passed through the column, methanol was the solvent used for cleaning. With the silica gel still packed in the column, methanol was passed through the column with the aid of vacuum and collected into a receiving flask. Once there is no colour in the methanol eluting off the column, all the methanol was then drained. The silica gel was then placed in the oven at 75 ^{o}C to be reactivated for 2 days. Ethyl acetate was used for the columns that only had the green/yellow diesel eluted through. Same as with methanol, ethyl acetate was eluted through the column, until there was no colour in the solvent. The silica gel was then placed in the oven at 75 ^{o}C for 2 days. These two types of silica gel were kept separated as they had different properties for separating diesel. The dark silica gel refers to the silica gel cleaned with methanol, because it is darker in colour then the silica gel cleaned with ethyl acetate, which will be referred to as light silica gel.

2.7 TAN Testing:

A solution of alcoholic KOH was prepared by weighing 1.40 g of KOH and dissolving it in 250 mL of isopropanol. A new solution of alcoholic KOH was prepared, and molarity standardized before any TAN testing. To determine the molarity of alcoholic KOH, 1.0 mL of 1 M HCl was diluted with 25 mL of isopropanol in a 250 mL beaker equipped with a stir bar and a conductivity probe. The “burette” shown in Figure 5 was filled with alcoholic KOH and was set to a constant drop rate by draining the syringe until the tube in the middle begins to bubble. The top stopcock is then set to the desired drop rate and the bottom stopcock is used as the open and close valve. The mass of the burette is recorded, as the difference in initial to final mass will be used to determine the amount of titrant added. The titration is performed using Logger Pro to make a graph of conductivity vs time, starting data collection at the same time the “burette” is opened. The mass of the “burette” is then recorded after the titration and equation 2 is used to determine molarity.

In a 250 mL beaker equipped with a stir bar and conductivity probe. 15-20 g of the diesel being tested is placed into the beaker and diluted with 25 mL of isopropanol. The burette with known concertation of alcoholic KOH is prepared as above and the titration is performed the same way on the diesel sample, except equation 1 is used instead. For each diesel sample, the TAN testing is performed in triplicate for better statistical results.

2.8 Reducing TAN Value:

Solid KOH:

In a 300 mL round bottom flask equipped with a stir bar, 60 g of purified green diesel produced from column V.2.2 was added along with 2.00 g (0.036 mol) of solid KOH. The mixture was then left to stir for 17 hrs. After 17 hrs the solution was now brown in colour and was worked up by washing with water and dried over $MgSO_4$ for 10 mins. The diesel was then vacuum filtered. The resulting diesel after work up was back to being green in colour and its TAN value was 1.68 mg of KOH per g of diesel from an original value of 8.31 mg of KOH per g of diesel.

Solid K_2CO_3:

In a 300 mL round bottom flask equipped with a stir bar, 60 g of green diesel was added along with 4.97 g (0.036 mol) of K_2CO_3. The mixture was stirred for 17 hrs and worked up by washing with water and drying over $MgSO_4$ for 10 mins. The diesel was collected *via* vacuum filtration. The diesel sample was then titrated. Compared to the KOH treatment, there was no colour change of the diesel throughout. The TAN value was determined to be 4.25 mg of KOH per g of diesel from an original value of 8.31 mg of KOH per g of diesel.

Solid $NaHCO_3$

In a 300 mL round bottom flask equipped with a stir bar, 60 g of green diesel was added along with 2.98 g (0.036 mol) of $NaHCO_3$. The mixture was stirred for 17 hrs before a work up of washing with water and drying over $MgSO_4$. The diesel was collected with vacuum filtration and was tested for its TAN value and was determined to be 3.00 mg of KOH per g of diesel from an original value of 8.31 mg of KOH per g of diesel.

Sat. Aqueous KOH:

60 g of green diesel was placed into a 300 mL round bottom flask equipped with a stir bar. A saturated solution (21.56 M) of aqueous KOH was prepared, and 60 g of sat. KOH solution was also added to the round bottom flask. The mixture was left to stir for 17 hrs. After the allotted time, stirring was stopped and the aqueous layer was allowed to separate from the diesel. The aqueous layer was then removed using a separatory funnel, and the diesel was then washed with water and dried over $MgSO_4$. The diesel was then collected with vacuum filtration and the TAN value was found to be 5.36 mg of KOH per g of diesel from an original value of 8.31 mg of KOH per g of diesel.

Sat. Aqueous KOH and $[N_{4444}][Cl]$:

60 g of green diesel was placed into a 300 mL round bottom flask equipped with a stir bar. 60 g of sat. KOH solution was added to the round bottom flask along with 0.6 g of $[N_{4444}][Cl]$. The solution was left to stir for 17 hrs. After the given amount of time, the stirring was stopped, and the aqueous layer was allowed to separate from the diesel. The two layers were then separated using a separatory funnel. The diesel was washed with water and dried over $MgSO_4$. The diesel was then collected using vacuum filtration and was tested for its TAN value, which was found to be 2.62 mg of KOH per g of diesel from an original value of 8.31 mg of KOH per g of diesel. The diesel was a brown colour similar to when the diesel was treated with solid KOH and a solid powder that was black in colour was observed on top of the aqueous layer seen in Figure 9.

Figure 9: Reaction flask of Sat. KOH Solution and PTC.

Sat. Aqueous KOH and $[N_{1111}][Cl]$:

60 g of green diesel was placed into a 300 mL round bottom flask equipped with a stir bar. 60 g of sat. KOH solution was added to the round bottom flask along with 0.6 g of $[N_{1111}][Cl]$. The solution was left to stir for 17 hrs. After the given amount of time the stirring was stopped. The aqueous layer was allowed to separate from the diesel. The two layers were then separated using a separatory funnel. The diesel was washed with water and dried over $MgSO_4$. The diesel was then collected using vacuum filtration and was tested for its TAN value and determined to be 3.42 mg of KOH per g of diesel from an original value of 8.31 mg of KOH per g of diesel.

Sat. Aqueous KOH and $[N_{2222}][Cl]$:

60 g of green diesel was placed into a 300 mL round bottom flask equipped with a stir bar. 60 g of sat. KOH solution was added to the round bottom flask along with 0.6 g of $[N_{2222}][Cl]$. The solution was left to stir for 17 hrs. After the given amount of time the stirring was stopped, and the aqueous layer was allowed to separate from the diesel. The two layers were then separated using a separatory funnel. The diesel was washed with water and dried over $MgSO_4$. The diesel was then collected using vacuum

filtration and was tested for its TAN value, which was found to be 2.77 mg of KOH per g of diesel from an original value of 8.31 mg of KOH per g of diesel.

6% Aqueous KOH and $[N_{4444}][Cl]$ at 50 ^{o}C:

60 g of green diesel was placed into a 300 mL round bottom flask equipped with a stir bar. 60 g of 6% KOH solution was added to the round bottom flask along with 0.6 g of $[N_{4444}][Cl]$. The flask was then purged with nitrogen gas and was heated to 50 ^{o}C. The solution was left to stir for 17 hrs. After the given amount of time the stirring was stopped, and the flask was removed from heating. The aqueous layer was allowed to separate from the diesel and to cool down. The two layers were then separated using a separatory funnel. The diesel was washed with water and dried over $MgSO_4$. The diesel was then collected using vacuum filtration and was tested for its TAN value, which was determined to be 1.69 mg of KOH per g of diesel from an original value of 3.20 mg of KOH per g of diesel.

6% Aqueous KOH at 50 ^{o}C:

60 g of green diesel was placed into a 300 mL round bottom flask equipped with a stir bar. 60 g of 6% KOH solution was added to the round bottom flask. The flask was then purged with nitrogen gas and was heated to 50 ^{o}C. The solution was left to stir for 17 hrs. After the given amount of time the stirring was stopped, and the flask was removed from heating. The aqueous layer was allowed to separate from the diesel and to cool down. Two layers were then separated using a separatory funnel. The diesel was washed with water and dried over $MgSO_4$. The diesel was then collected using vacuum filtration and was tested for its TAN value, which was found to be 2.51 mg of KOH per g of diesel from an original value of 3.20 mg of KOH per g of diesel.

Solid KOH at 50 ^{o}C:

60 g of green diesel was placed into a 300 mL round bottom flask equipped with a stir bar. 2.00 g of solid KOH was added to the round bottom flask. The flask was then purged with nitrogen gas and was heated to 50 ^{o}C. The solution was left to stir for 17 hrs. After the given amount of time the stirring was stopped and removed from heating to cool down. The diesel was separated from the KOH by washing with water and the two layers were separated by using a separatory funnel. The diesel was then dried over $MgSO_4$. The diesel was then collected using vacuum filtration and was tested for its TAN value, which was determined to be 2.43 mg of KOH per g of diesel from an original value of 3.20 mg of KOH per g of diesel.

Sat. KOH and $[N_{4444}][Cl]$ 50 ^{o}C:

60 g of green diesel was placed into a 300 mL round bottom flask equipped with a stir bar. 60 g of sat. KOH solution was added to the round bottom flask along with 0.6 g of $[N_{4444}][Cl]$. The flask was then purged with nitrogen gas and was heated to 50 ^{o}C. The solution was left to stir for 17 hrs. After the given amount of time the stirring was stopped, and the flask was removed from heating. The aqueous layer was allowed to separate from the diesel and to cool down. Two layers were then separated using a separatory funnel. The diesel was washed with water and dried over $MgSO_4$. The diesel was then collected using vacuum filtration and was tested for its TAN value and was found to be 2.14 mg of KOH per g of diesel from an original value of 3.20 mg of KOH per g of diesel.

6% Aqueous KOH and $[N_{4444}][Cl]$ at 70 ^{o}C:

60 g of green diesel was placed into a 300 mL round bottom flask equipped with a stir bar. 60 g of 6% KOH solution was added to the round bottom flask along with 0.6 g of $[N_{4444}][Cl]$. The flask was then purged with nitrogen gas and was heated to 70 ^{o}C. The solution was left to stir for 17 hrs. After the

given amount of time the stirring was stopped, and the flask was removed from heating. The aqueous layer was allowed to separate from the diesel and to cool down. Two layers were then separated using a separatory funnel. The diesel was washed with water and dried over $MgSO_4$. The diesel was then collected using vacuum filtration and was tested for its TAN value and was determined to be 2.40 mg of KOH per g of diesel from an original value of 4.75 mg of KOH per g of diesel.

Sat. KOH and $[N_{4444}][Cl]$ at 70 ^{o}C:

60 g of green diesel was placed into a 300 mL round bottom flask equipped with a stir bar. 60 g of sat. KOH solution was added to the round bottom flask along with 0.6 g of $[N_{4444}][Cl]$. The flask was then purged with nitrogen gas and was heated to 70 ^{o}C. The solution was left to stir for 17 hrs. After the given amount of time the stirring was stopped, and the flask was removed from heating. The aqueous layer was allowed to separate from the diesel and to cool down. Two layers were then separated using a separatory funnel. The diesel was washed with water and dried over $MgSO_4$. The diesel was then collected using vacuum filtration and was tested for its TAN value and was determined to be 2.63 mg of KOH per g of diesel from an original value of 4.75 mg of KOH per g of diesel.

Solid KOH at 70 ^{o}C:

60 g of green diesel was placed into a 300 mL round bottom flask equipped with a stir bar. 2.00 g of solid KOH was added to the round bottom flask. The flask was then purged with nitrogen gas and was heated to 70 ^{o}C. The solution was left to stir for 17 hrs. After the given amount of time the stirring was stopped and removed from heating to cool down. The diesel was separated from the KOH by washing with water and the two layers were separated by using a separatory funnel. The diesel was then dried over $MgSO_4$. The diesel was then collected using vacuum filtration and was tested for its TAN value and

was found to be 2.67 mg of KOH per g of diesel from an original value of 4.75 mg of KOH per g of diesel.

6% Aqueous KOH and [N_{4444}][Cl] at 70 ^{o}C with Clear Diesel:

60 g of clear diesel was placed into a 300 mL round bottom flask equipped with a stir bar. 60 g of 6% KOH solution was added to the round bottom flask along with 0.6 g of [N_{4444}][Cl]. The flask was then purged with nitrogen gas and was heated to 70 ^{o}C. The solution was left to stir for 17 hrs. After the given amount of time the stirring was stopped and the flask was removed from heating. The aqueous layer was allowed to separate from the diesel and to cool down. Two layers were then separated using a separatory funnel. The diesel was washed with water and dried over $MgSO_4$. The diesel was then collected using vacuum filtration and was tested for its TAN value and was determined to be 1.21 mg of KOH per g of diesel from an original value of 1.78 mg of KOH per g of diesel.

5% Aqueous KOH and [N_{4444}][Cl] Solution at 70 ^{o}C with Clear Diesel:

60 g of clear diesel was placed into a 300 mL round bottom flask equipped with a stir bar. 60 g of 5% KOH and 5% [N_{4444}][Cl] solution was added to the round bottom flask. The flask was then purged with nitrogen gas and was heated to 70 ^{o}C. The solution was left to stir for 2 hrs. After the given amount of time the stirring was stopped and the flask was removed from heating. The aqueous layer was allowed to separate from the diesel and to cool down. Two layers were then separated using a separatory funnel. The diesel was washed with water and dried over $MgSO_4$. The diesel was then collected using vacuum filtration and was tested for its TAN value, which was found to be 1.51 mg of KOH per g of diesel from an original value of 1.78 mg of KOH per g of diesel.

3. Results and Discussion:

3.1 Charcoal and Celite:

In organic chemistry procedures, to remove colour impurities from organic molecules, charcoal is commonly used as an adsorbent. Since one of the tasks assigned to improve the diesel is to improve the colour and smell, the idea to use charcoal to remove coloured impurities came to mind. This was attempted with mixing raw diesel without any solvent with 2 g of charcoal for 2 hours. It was found that the raw diesel forms a thick fluid solid with the charcoal that was hard to filter *via* gravity filtration. To help with the filtration, chloroform was used to increase the rate of flow. Chloroform was used as it was the only solvent known at the time of this experiment that the raw diesel was soluble in. After all of the diesel was filtered and the chloroform was removed, the charcoal did not have an effect on the diesel as the colour and smell remained the same. To not be deterred by these results, raw diesel was dissolved in chloroform and stirred for 2 hours with 2 grams of charcoal then filtered through a Celite bed. This was done as the Celite may keep the colour impurities from filtering through. After the solvent was removed, this method also did not have any effect on the colour and smell and the idea of using charcoal to improve colour and smell was abandoned and the focus was changed to use column chromatography in removal of impurities.

3.2 Column Optimization:

Column chromatography is a method of separating mixtures of compounds from one another using their differences in polarity. As the mixtures of compounds separate on the column, the least polar molecules will elute off the column first using normal phase silica gel. The more polar molecules will have better interaction with the silica gel slowing their travel down the column compared to the non-polar molecules that will have less interactions. Using chromatography, the raw diesel can be passed through and separated into its different fractions. Since diesel is composed of non-polar hydrocarbons, molecules like organosulfur molecules will be relatively more polar. When raw diesel is passed through a column of silica gel, the more polar organosulfur molecules with be retained by the column and the diesel hydrocarbons will elute first. The issue with trying to remove sulfur is that at Saint Mary's University the chemistry facilities do not have the ability to detect these amounts of sulfur. This causes an issue as the performance of the column cannot be judged in house and the detection was to be done by an outside company, which will take time for results. The first columns performed showed that there were significant improvements in the colour and smell of the diesel. To not have any delay in progress in the research, the change in colour and smell will be used in judging if the column had a beneficial effect on the diesel.

To begin, column optimization at a small scale is done before doing any large-scale experiments to prevent waste of materials (Table 1). In the optimization of the column two different variables were explored, which were the stationary phases and solvents. Changing the stationary phases will change the polarity of the column, which will result in different separation of the diesel. Different solvents also have differences in polarity and will have an effect on the rate at which the raw diesel will elute from the column. To keep conditions constant, a 2.54 cm diameter column filled with 15 cm of stationary phase and 25 mL of raw diesel was used. In Figure 10, samples show the change in colour after being eluted from the column, where vial 1 is the raw diesel used for comparison.

Table 1: Column optimization.

Column Version	Solvent	Stationary Phase	Number of Fractions	Colour of Fractions
V.1.0	Chloroform	Silica Gel	2	Orange and Brown
V.1.1	Chloroform	Alumina	2	Yellow and Brown
V.1.2	THF	Alumina	2	Yellow and Brown
V.1.3	Diethyl Ether	Alumina	2	Yellow and Brown
V.1.4	Hexanes	Alumina	3	Green, Orange, and Brown
V.1.5	Pentane	Alumina	0	N/A
V.1.6	Hexanes	Silica Gel	3	Green, Orange and Brown

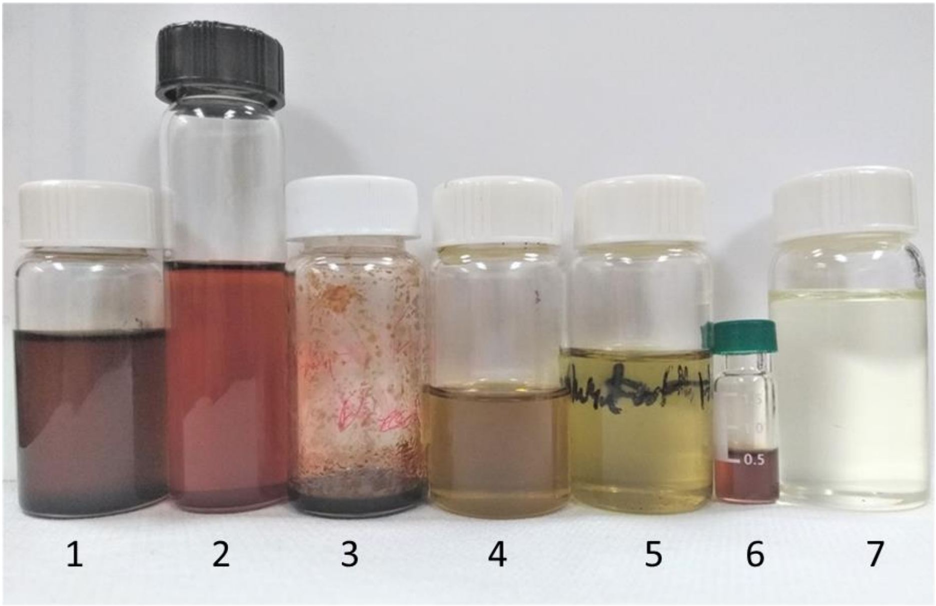

Figure 10: Vials for column optimization.

The first stationary phase used in the column optimization was silica gel. The first solvent used was chloroform as mentioned above, due to its ability to solubilize the raw diesel. In this first column, the raw diesel visibly separated into two fractions, one orange colour and the other a dark brown colour. The orange fraction eluted from the column first and the second did not move through the column and ethyl acetate was needed to elute the fraction. After the solvent was removed, the resulting colours were the orange colour seen in vial 2 and the dark brown which is vial 3. Compared to the raw diesel, the colour did not change in a large way, and the smell was still the same, but it changed enough to show that there is potential in this method. The second dark brown fraction needed a stronger polarity solvent to be eluted from the column, showing that this fraction may contain polar molecules such as carboxylic acids and organosulfur molecules. To continue the optimization, the stationary phase was changed to activity I alumina. Keeping the same conditions and chloroform as solvent, a different coloured fraction was observed. The raw diesel separated into two fractions again, except the first fraction was no longer orange but yellow in colour. This fraction is seen as vial 4 in Figure 10 and the second fraction, similar to the first column, needed ethyl acetate to elute, which was the same as vial 3. Changing the stationary phase to alumina had the beneficial effect of lightening the colour of the diesel and removing some of the stronger smells. As silica gel and alumina were the only stationary phases easily available in the lab, alumina was chosen to move forward with solvent optimization.

As chloroform is known to be a polar solvent, the separation of the raw diesel can be improved by using less polar solvents to slow down the rate at which molecules will elute from the column. To try to maximize separation, pentane was explored as a solvent with alumina as the stationary phase. Pentane is the least polar solvent that can be used in our lab and unfortunately did not elute any of the diesel through the column. The next solvents used were THF and diethyl ether, as these two solvents have a lower polarity than chloroform, however these two solvents did not change the separation and had the same colour fractions appearing.

The last solvent tried was hexanes as this solvent is slightly more polar than pentane. Out of all solvents tested, hexanes gave the best results, separating the diesel into three fractions. The first to be eluted from the column was green in colour and can be seen in vial 5. The second was yellow on the column, but after solvent was removed the fraction was an orange colour seen in vial 6. The last fraction is the same as all the other last fractions, needing ethyl acetate to elute from the column and is the same as vial 1. With the improvement in colour also came improvement in the smell: the green fraction has a petroleum like aroma, compared to the campfire odour of the raw diesel. The hexanes worked the best as it is a non-polar solvent similar to the hydrocarbons of diesel, which would be more favorable to elute with the hexanes compared to being on the polar surface of the column. This allows a better separation of the raw diesel compared to more polar solvents. Hexanes are also more polar than pentane, which enables the hexanes to elute the diesel where the pentane cannot. The last thing done in optimization was trying the hexanes with silica gel as a stationary phase. The results of this were the same compared to alumina as the stationary phase. Since silica gel was more available compared to alumina, moving onwards to large scale columns silica gel was the chosen stationary phase.

3.3 Large Scale Columns:

Table 2: Large scale column.

Column Version	**Diameter** (cm)	**Amount of Silica Gel** (g)	**Raw Diesel** (mL)	**Green/Clear Diesel**(mL)	**Solvent**	**Vacuum**	**% Recovery**
V.2.0	2.54	104	200	130 Green	Hexanes	No	65%
V.2.1	5.08	450	500	350 Green	Hexanes	No	70%
V.2.2	7.62	450	500	350 Green	Hexanes	Yes	70%
V.2.3	7.62	450	500	50 Clear	No	Yes	10%
V.2.4	7.62	150	500	175 Clear	No	Yes	35 %

Large scale purifications are important as all the TAN reduction studies will be performed on the purified diesel. Being able to produce the cleaned diesel in bulk will save on time better used for more experiments. To begin, column V.2.0, which is 5.08 cm in diameter and contains 30 cm of silica gel was used to separate 200 mL of raw diesel (Table 2). This column can be seen in Figure 11. We were able to recover about 130 mL of the 200 mL used, a recovery of about 65% This column shows that it is possible to scale up in size, and that over half the diesel can be recollected as the green colour diesel. The issue is that at this scale, the column needs to be performed many times as 60 g of diesel is used in each TAN reduction reaction, which is around 80 mL of green diesel. The column V.2.0 was then scaled up to a larger column (V.2.1) that was 7.62 cm in diameter filled with 500 g of silica gel, which is also seen in Figure 11. This column was designed for being able to separate 500 mL of raw diesel, and the amount recollected as green diesel was about 350 mL, a recovery of 70%. This column was able to collect more green diesel, probably due to the diesel having to travel farther in the 7.62 cm column, allowing more separation. A problem with this column is the large amount of solvent (3-4 L) used to elute the material. To save on the amount of solvent being wasted the hexanes is recollected from the rotary evaporator. What is also found was that some of the hexanes gets trapped in the green diesel, which is removed under Schlenk line vacuum, collected, and reused.

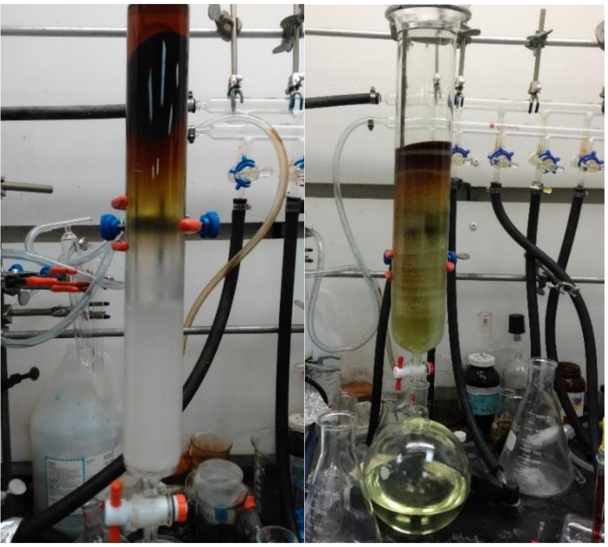

Figure 11: Columns for V.2.0 and V.2.1.

In the development of the large-scale purification method, a risk arises with running the column, which was pouring solvent above the head as the column height got taller. To prevent any solvent from being poured down the arms or on the head, a tube was attached to the top of the column that ran down to a solvent reservoir. As the diesel elutes from the column this would create a vacuum that can pull the solvent up from the reservoir into the column. A vacuum in the form of an aspirator pump was attached to the bottom of the column with a trap in between. Applying a small vacuum, the eluents from the column are collected in the trap (Figure 7). This made separating the diesel easier as time to run the column was decreased and without the need to constantly top up the solvent, column V.2.2 can be left to run with minimal supervision. Flash chromatography was not considered as the column did not have the capacity to hold 3-4 L of hexanes. Refilling the column would be required, defeating the original purpose of this method.

With the large amount of solvent being used to perform these columns, to be able to run he column using less solvent will be a huge benefit. Column V.2.3 is 7.62 cm in diameter and contains 450 g of dry silica gel. When 500 mL of raw diesel was added, the fuel does not elute through the column. When adding the aspirator vacuum, the rate increased slightly but was still considerably slower compared to using solvent. A stronger vacuum was then applied using the Schlenk line vacuum, which caused the diesel to elute at a rate comparable to if there was solvent. As the diesel eluted into the column, the same set of fractions seen with hexanes was visible. Once all the diesel eluted into the column, the rate of diesel traveling through got considerably slower.

With 450 g of silica gel, the column was too long for a large amount of purified diesel to be collected. Column V.2.4 uses the same method with 150 g of silica gel and 500 mL of raw diesel. Under this set-up, a new diesel fraction was obtained that is clear in colour (seen in Figure 12). This fraction is the first to elute from the column and has a diesel-like smell and makes up the majority of the raw diesel. What elutes after the clear diesel is the green/yellow coloured fraction previously observed, which can be collected and passed through another column to collect more clear diesel.

Figure 12: Clear diesel.

3.4 Reusability:

With performing many columns, the amount of silica gel being discarded as waste started to become a large amount. To be more efficient and reduce waste, methods of cleaning the silica gel for reuse were explored. Two methods were developed for recycling the silica gel; the method used depends on what has been passed through the silica gel previously. If the raw diesel was passed through a column, methanol is used and if the green/yellow diesel was passed through, ethyl acetate is used. The different solvents for cleaning the silica gel were used as the brown material from the raw diesel column only can be removed with methanol. For both solvents, the procedure is the same; with the used silica gel in the column attached to the aspirator pump, the required solvent is eluted through the column and collected in the trap. Solvent was added until there was no colour in the solvent at the end of the column. The silica gel is then placed into an oven for 2 days to reactivate the silica gel by removing remaining solvent and water molecules. Heating in the oven for 2 days is important as air-dried silica results in no separation of the raw diesel. The silica gel cleaned with methanol has a dark colour compared to the silica gel cleaned with ethyl acetate; the two types of recycled silica gel are kept separate as they have different activity.

The overall activity of the cleaned silica gels compared to fresh silica gel does not have large differences; however, over many regenerations cycles the silica gels do become inactive.

3.5 Capacity and Two Stage Columns:

Table 3: Column capacity.

Column Version	**Type of Silica Gel**	**Total Amount of Raw Diesel** (mL)
V.2.6	Fresh	800 mL
V.2.7	Light	750 mL
V.2.8	Dark	600 mL

With the two types of reused silica gel, the loss of efficiency is important for the total amount of diesel that can be passed through before the column is not usable. 100 g of each type of silica was placed in a 5.08 cm-diameter column. Using the Schlenk line vacuum, 500 mL of raw diesel was placed on top on the column first and eluted through. Once all the diesel was eluted into the column, 50 mL of raw diesel was added. This was repeated until brown colour was eluting from the column. The fresh silica gel had the best performance, being able to handle 800 mL of raw diesel before it was not usable (Table 3). The second best was the light silica gel, being able to handle 750 mL of raw diesel, and the dark colour silica gel had the worst activity of only 600 mL. Unsurprisingly the reused silica gel has less activity compared to fresh silica gel. This loss in activity can be from the loss of active sites on the surface of the silica gel, which cannot be freed up by cleaning with solvents. To maximize the total amount of diesel that can be separated, two-stage columns were designed. These two-stage columns (Figure 8) allow more diesel to be separated, with the first column removing the bulk of the contaminants before becoming unusable, while the second column can continue separating the diesel. What was found to work the best was to have a collection flask in between the two columns, so that large amounts of diesel being purified can be added to the second column at once. This gave a better separation compared to the other column designs with multiple columns. With this method, over 1.5 L of diesel was separated with two columns having 75 g of silica gel a piece**.** The diesel that was separated had the TAN values determined and will be used for TAN reduction experiments.

3.6 TAN Reduction:

Table 4: Base optimization.

Sample	**TAN** (mg of KOH/ 1g of diesel)
Raw Diesel untreated	6.57 (±0.49)
Green Diesel (Column)	8.31 (±0.53)
Clean Diesel treated with 0.036 mol of KOH	1.68 (±0.35)
Clean Diesel treated with 0.036 mol of K_2CO_3	4.25 (±0.90)
Clean Diesel treated with 0.036 mol of $NaHCO_3$	3.00 (±0.21)

Using the titrator that was previously described, the TAN value of the raw diesel was determined to be 6.57 mg of KOH per g of diesel; this agrees with the value provided by the company of between 6.5-7 mg of KOH per g of diesel (Table 4). To determine if this titration method is valid, standardization was performed using known concentrations of strong and weak acids, such as HCl and acetic acid. TAN values will be determined in isopropanol, therefore standardization tests with both water and isopropanol were done. Through these tests, the measured values agreed with the known values and this method was therefore expected to be reliable. The TAN value was then determined for the green clean diesel produced by column chromatography, which turned out to be 8.31 mg of KOH per g. The increase of the TAN value could be from the acidity of the silica gel being transferred to the diesel or could be an increase in concentration of acids in the clean diesel. Later results determine the TAN value of the green diesel to be less than 0.03 mg of KOH per g of diesel (*vide infra*).

Three different inorganic bases were used to see which would be the best base for TAN reduction. Equal mole equivalents of each base were used on 60 g of green clean diesel with the same reaction conditions. Out of the three bases used, KOH, K_2CO_3 and $NaHCO_3$, the strongest base of KOH had the greatest effect on the TAN value. The initial value of the clean green diesel was 8.31 mg of KOH per g, which was reduced to 1.68 mg of KOH per g, a reduction of 80 %. It makes sense that the stronger of the bases would have the greatest reduction of the TAN value compared to weaker bases under the same conditions. Inorganic bases such as KOH do have the problem of being non-soluble in the diesel. The rate at which the acids are neutralized is related to the surface area of the KOH pellets. Powdered KOH is more effective compared to solid pellets since the powder has a much higher surface area to volume ratio, thus allowing larger amounts of KOH to react. Organic bases are suitable as they are soluble in the diesel, allowing all the base to be accessible for reaction. However organic bases were not tested, as these bases are weaker compared to KOH.

After determining the optimal base for the reduction of the TAN value, different methods on delivering the base to the diesel were then explored. The first method tested was adding the solid directly into the diesel and allowing it to stir. As mentioned above, the rate determining step of using solid KOH is the surface area available to react.[45] Another method on delivering the KOH to the diesel is to use an aqueous solution. The carboxylate ions that are formed will be more soluble in the aqueous phase, which will transfer into the aqueous phase. The issue with KOH in an aqueous solution is that transferring the OH^- ions from its more favorable aqueous phase to the less favorable diesel phase is a slow process. To help combat this problem, phase transfer catalysts (PTCs) were used to aid in the solubility of the OH^- ions.[46] The PTCs are organo-ammonium salts that are soluble in both an organic phase and aqueous phase, depending on the anion. The PTCs that were used are $[N_{1111}][Cl]$, $[N_{2222}][Cl]$, and $[N_{4444}][Cl]$. These PTCs were tested under the same conditions of sat. KOH solution (21.56 M) and with a 0.1 w/w% of PTC, as seen in Table 5. The PTCs were shown to have a positive effect on the reduction of TAN value. With only using sat. KOH solution, the percent reduction was 35.5%. Comparing this to the lowest percent reduction when PTCs were used, which was 58.8 % for $[N_{1111}][Cl]$. The benefit of the PTCs is the low amount that was used, which was 0.06 g of PTCs for 60 g of diesel. Out of the PTCs that were used, the best performing was the [N$_{4444}$][Cl] with a percent reduction of 68.5 %. The [N$_{2222}$][Cl] catalyst had performed similarly to [N$_{4444}$][Cl] with a percent reduction of 66.6 %. The [N$_{4444}$][Cl] catalyst was chosen to be carried forward for TAN reduction as it provided the greatest percent reduction. Using the PTCs with sat. KOH solution a solid can be seen between the aqueous phase and the diesel phase (see Figure 9). This could be from the PTC not being able to dissolve completely as the amount of KOH makes the aqueous phase overly saturated.

Table 5: Optimization of PTC on green diesel.

PTC	**Starting TAN**	**TAN** (mg of KOH/ 1 g of diesel)	**%Reduction**
None	8.31 (±0.53)	5.36 (±0.21)	35.5 (±7.2)
[N$_{1111}$][Cl]	8.31 (±0.53)	3.42 (±0.36)	58.8 (±8.6)
[N$_{2222}$][Cl]	8.31 (±0.53)	2.77 (±0.06)	66.6 (±7.7)
[N$_{4444}$][Cl]	8.31 (±0.53)	2.62 (±0.19)	68.5 (±8.1)

Table 6: Condition optimization for TAN value reduction on green diesel. PTC as [N$_{4444}$][Cl].

Conditions	**Starting TAN**	**TAN** (mg of KOH/ 1 g of diesel)	**% Reduction**
2.0 g solid KOH	8.31 (±0.53)	1.68 (±0.35)	79.8 (±9.2)
Sat. KOH	8.31 (±0.53)	5.36 (±0.21)	35.5 (±7.2)
Sat. KOH and 0.1% PTC	8.31 (±0.53)	2.62 (±0.19)	68.5 (±8.1)
2.0g solid KOH at 50 °C	3.20 (±0.11)	2.43 (±0.20)	24.1 (±7.2)
6% wt/v KOH at 50 °C	3.20 (±0.11)	2.51 (±0.01)	21.6 (±3.5)
6% wt/v KOH at 50 °C and 0.1% PTC	3.20 (±0.11)	1.69 (±0.06)	47.2 (±4.2)
Sat. KOH at 50 °C and 0.1% PTC	3.20 (±0.11)	2.14 (±0.12)	33.1 (±5.2)
2.0 g of solid KOH at 70 °C	4.75 (±0.61)	2.67 (±0.06)	43.8 (±14.1)
6% wt/v KOH at 70 °C and 0.1% PTC	4.75 (±0.61)	2.40 (±0.15)	49.7 (±14.7)
Sat. KOH at 70 °C and 0.1% PTC	4.75 (±0.61)	2.63 (±0.05)	44.6 (±14.1)

Many different conditions for TAN reduction have been attempted to reach the ASTM standard of 0.5 g of KOH per g of diesel. As seen in Table 6, different conditions such as the concentration of KOH solution, temperature, and solid KOH or PTC were used for optimization. Between experiments, the initial TAN value of the green diesel was different. The change in the initial TAN value was always observed when a new sample of diesel was prepared with column chromatography. Since there is a range in the TAN value of the initial green diesel, the total percent reduction of acidity will be used as the measure of effectiveness of each condition. In Table 3, the PTC used was the $[N_{4444}][Cl]$ catalyst, as it had the best performance. Heated experiments were placed under a nitrogen atmosphere to prevent combustion of the diesel, because the temperatures were above the diesel flashpoint.

Out of all the reaction conditions tested, those that had the highest % reduction in the TAN value was 2.0 g of solid KOH at room temperature with a percent reduction of 79.8%. In Table 6, what is seen is that the TAN value tends towards a limit between 2.6-1.6 mg of KOH per g of diesel. Using solid KOH or a solution of KOH with the PTC had similar effects on the TAN value and can reach the same minimal value. Even at the increased temperatures the TAN value does not get below the limit of 1.6 mg of KOH per g of diesel. This presents the issue of not being able to reach the standard of 0.5 mg of KOH per g of diesel. Better conditions for reducing the TAN value will be needed to lower the green diesel to the standard value.

Table 7: TAN reduction on clear diesel.

Conditions	**Starting TAN**	**TAN** (mg of KOH/ 1 g of diesel)	**% Reduction**
None	1.78 (±0.06)	1.78 (±0.06)	N/A
6% wt/v KOH at 70 °C and 0.1% PTC	1.78 (±0.06)	1.21 (±0.01)	32.0 (±3.6)
5% wt/v of KOH and PTC at 70 °C 2hrs	1.78 (±0.06)	1.51 (±0.17)	15.2 (±4.8)

In the above column optimization studies, a clear, colourless diesel fraction was obtained. The TAN value of this new fraction was found to be much lower than the initial values of the green diesel at 1.78 mg of KOH per gram of diesel seen in Table 7. An experiment to reduce the TAN value of the clear diesel was done under previously described conditions. Given the limit to TAN value reduction described above for the green diesel fraction, we did not expect a significant impact on the TAN value for the clear fraction. When 6 % w/v of KOH solution with a 0.1 % PTC was used, the TAN value was lowered from 1.78 to 1.21 mg of KOH per g of diesel, a percent reduction of 32.0 %, a sizable improvement but still not meeting the ASTM standard value of 0.5 mg of KOH per g of diesel. Increasing the amount of PTC to 5% wt/v showed some promise by allowing a 15.2% reduction in TAN in only 2 hours compared to the 17 hours normally used.

While the above studies were being conducted, a sample of the green diesel that had been provided to our industrial collaborators was analyzed at a contracted lab. The TAN value of the green diesel was found to be less than 0.03 mg of KOH per g of diesel. This was great news, demonstrating that the TAN value was already 10 times below the ASTM D975 standard limit of 0.5 mg of KOH per g of diesel upon exiting the purification column. However, this result also means, there is a systematic problem with the titration system developed here, given that the TAN values obtained are off by two orders of magnitude. Similarly, the clear diesel had a TAN value of 0.0561 mg of KOH per g of diesel. The observation that the column lowers the TAN value makes sense, as the acids expected in the diesel are carboxylic acids. These acids are polar and should be retained by the column. A clear diesel sample was not prepared to determine the sulfur content in this fraction. Knowing this value would give insight to how much the colour of the diesel is correlated to sulfur content.

4. Conclusion:

Using column chromatography, the colour and the smell of the raw diesel was greatly improved. The colour was no longer a dark brown colour and can be cleaned to a clear version that resembles diesel that can be purchased at a gas pump. The fuel can also be collected in a green version that reaches the same quality standards. The smell no longer resembles a strong camp fire burning smell; the clear and green versions of the diesel have the classic petroleum smell of hydrocarbons. The purification columns were optimized to have silica gel as the stationary phase. The column was built to be able to feed itself using the aspirator pump by drawing the solvent from a reservoir. Using the idea of a vacuum pump, a column was designed to have the diesel to act as the solvent. Using this method, a clear diesel product was collected. Larger-scale columns were developed that can separate large amounts of raw diesel in one experiment. To be greener, the solvent and silica gel can be collected and cleaned for reuse, resulting in little waste.

The conductivity titrator that was used in determining the TAN value of diesel was misleading, as the values determined using the titrator were off by a factor of 100. The TAN reduction experiments were not needed as the diesel from purification already had a TAN value of less than 0.05 mg of KOH per g of diesel. This was determined by an outside source chemical testing company. The TAN value was reduced below the ASTM D975 standard of 0.5 mg of KOH per g of diesel from its initial value of about 7 mg of KOH per g of diesel.

Three out of the four goals of the research project were achieved. The colour and smell were improved, and the TAN value was brought below the standard value, with the total percent reduction of 99.7%. The only research goal that was not achieved was reducing the sulfur content. Column chromatography did not obtain the desired results of lowering the sulfur content. In fact, the sulfur was increased from its initial value. Overall column chromatography is a useful tool in the refining of diesel by being able to remove organic acids to lower the TAN value considerably. This can be economical as all the components of the column can be recycled and reused saving on costs. This method needs to be explored more, as of writing this thesis there are no publications on reducing the TAN value using column chromatography.

5. Future work:

More work needs to be done to improve the titration set up to obtain accurate results. Things can be done to drop the variability of the total amount of KOH added. Controlling the drop sizes of the KOH solution will give a better constant addition to accurately control the total amount of base being added. This can be done by using needles that will give consistent drop size, with different sized needles that can control the amount being added per drop. The drop rate can be changed to allow more time for the drop to diffuse into the diesel. Also, the reaction of the KOH with organic acids could be slow and giving more time in between addition of drops can allow that reaction to occur. Another way is to use a weaker concentration of alcoholic KOH solution. Changing the solvent that the diesel is dissolved in could have an effect. This could result in better conductivity giving increased detection.

More research can be done on column optimization. Optimization can consist of the ability to separate larger amounts of raw diesel into clear or green diesel. Maximizing the total amount of diesel that can pass through the silica gel and the total amount of times the silica gel can be reused will need to be explored. More research can be done on the column ability to reduce the TAN value. Questions like "what is the highest TAN value a column can handle", "how many times can this be reused", "how low can the TAN value be reduced", and "can the organic acids be collected?" can all be explored. As no published work has been done as of writing this thesis, this can be a great avenue for research moving forward.

One of the major issues of the research is that the sulfur content was not reduced below the standard of 15 ppm. More techniques need to be applied to the diesel to bring the levels down. Methods that were mentioned in the introduction can be done to see if the sulfur can be reduced. A new method can be developed, or column chromatography can be optimized for sulfur removal.

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