SULFONATED POLYETHER ETHER KETONE AS A SOLID ACID CATALYST FOR TRANSESTERIFICATION REACTIONS

POLYÉTHER ÉTHER CÉTONE SULFONÉ EN TANT QUE CATALYSEUR ACIDE SOLIDE POUR LES RÉACTIONS DE TRANSESTERIFICATION

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Abstract

Biodiesel is an environmentally friendly, low emission, direct replacement for diesel fuel. In this work, Sulfonated polyether ether ketone (SPEEK) was used as a catalyst in transesterification reactions, in order to explore the possibility of using SPEEK for the processing of biodiesel. SPEEK is a polymer with hygroscopic and acidic properties that increases with the degree of sulphonation (DS) of the polymer. SPEEK with a DS of 1.0 (100% sulphonated) dissolves in hot water while SPEEK with a DS lower than 0.4 does not dissolve in most organic solvents including methanol. All SPEEK used in this work was produced from the sulphonation of PEEK in concentrated sulphuric acid and characterized by the author. Transesterification reactions were conducted in a batch reactor at 50^{o}C with triacetin, a short chain triglyceride, and methanol using SPEEK as a homogeneous catalyst and as a heterogeneous catalyst in the form of SPEEK/PEEK hybrid pellets. SPEEK with a DS of 1.0 demonstrated the same catalytic properties as sulphuric acid at same normality, in a transesterification reaction. Catalyst pellets were produced with a skin of SPEEK and a core of PEEK. The DS at the surface of the pellets was evaluated to be 0.36 based on elemental analysis performed using Energy Dispersive Spectroscopy. The SPEEK pellets used as a heterogeneous catalyst displayed slower transesterification kinetics due to the reduced availability of catalytic sites limited to the surface area of the pellets. It was found that the SPEEK catalyst pellets gradually lost their catalytic effectiveness due to observable degradation of their surface area caused by grinding of the pellets during mixing in the reaction vessel. The activation energy of the processed SPEEK was determined to be 78 kJ/mol. The sulphonation reaction conversion was also modelled by adapting existing equations to the conditions used in this research.

Résumé

Le biodiesel est un produit de remplacement direct du diésel aussi plus respectueux de l'environnement. Dans ce travail, le polyéther éther cétone sulfoné (SPEEK) a été utilisé comme catalyseur dans les réactions de transestérification, afin d'explorer la possibilité d'utiliser le SPEEK afin de produire du biodiesel. Le SPEEK est un polymère aux propriétés hygroscopique et acide qui augmentent avec le degré de sulfonation (DS) du polymère. Le SPEEK avec un DS de 1,0 (100% sulfoné) se dissout dans l'eau chaude tandis que le SPEEK avec un DS inférieur à 0,4 ne se dissout pas dans la plupart des solvants organiques, comme le méthanol. Tout le SPEEK utilisé dans ce travail a été produit à partir de la sulfonation du PEEK dans de l'acide sulfurique concentré et caractérisé par l'auteur. Des réactions de transestérification ont été conduites dans un réacteur discontinu à 50 ° C avec de la triacétine, un triglycéride à chaîne courte et du méthanol en utilisant le SPEEK comme catalyseur homogène et comme catalyseur hétérogène sous la forme de pastilles hybrides SPEEK / PEEK. SPEEK avec un DS de 1,0 a démontré les mêmes propriétés catalytiques que l'acide sulfurique à la même normalité, dans une réaction de transestérification. Des pastilles de catalyseur ont été produites avec une peau de SPEEK et un noyau de PEEK. Le DS à la surface des pastilles a été évalué à 0,36 sur la base de l'analyse élémentaire réalisée en utilisant la spectroscopie à dispersion d'énergie. Les pastilles de SPEEK utilisées comme catalyseur hétérogène présentaient une cinétique de transestérification plus lente en raison de la disponibilité réduite de sites catalytiques limités à la surface des pastilles. Il a été trouvé que les pastilles de catalyseur de SPEEK perdaient progressivement leur efficacité catalytique en raison de la dégradation observable de leur surface provoquée par le broyage des pastilles pendant le mélange dans le réacteur discontinu. L'énergie d'activation du SPEEK produit a été déterminée comme étant de 78,37 kJ/mol. La conversion de la réaction de sulfonation a également été modélisée en adaptant des équations connues aux conditions utilisées dans cette recherche.

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List of Abbreviations

Ar – Aromatics

Cs – Sulphuric acid Constant

DG – Diglyceride

DS – Degree of Sulphonation

Ea – Activation Energy

EDS – Energy Dispersive Spectroscopy

F-Gases – Fluorinated Gases

FAME – Fatty Acid Methyl Ester

FFA – Free Fatty Acid

GHG – Green House Gas

Gly – Glycerol

MeOH – Methanol

TG – Triglyceride

MG – Monoglyceride

NMR – Nuclear Magnetic Resonance

PEEK – Polyether Ether Ketone

SEM – Scanning Electron Microscope

SPEEK – Sulfonated Polyether Ether Ketone

1 Introduction

Despite a growing number of mitigation policies, Green House Gas (GHG) emission growth has accelerated over the last decade [1]. The consequences of increasing amounts of greenhouse gases in the atmosphere are dire. They include increased average global temperature, rising sea levels, stronger storms, and ocean acidification. These effects will have a large impact on the human population [2]. In order to reverse this trend, new low emission technologies need to become cost competitive when compared to business as usual. In order to effectively reduce GHGs it is necessary to determine their source. Figure 1 outlines the different GHGs that are emitted, as well as the main sources for CO_2.

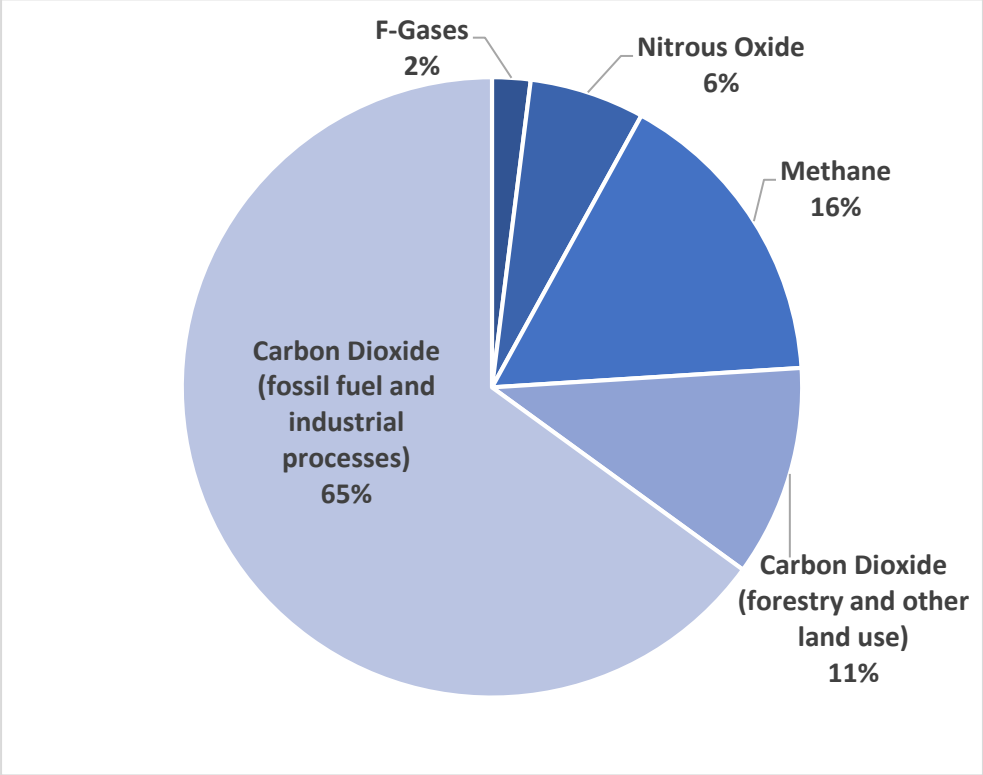

Figure 1: Greenhouse Gas Emissions, by type and source. Measured by Gt of CO2 equivalent/yr. Reproduced from [1].

CO_2 emissions account for 76% of the GHGs emitted each year, of which fossil fuel and industrial process make up the majority. In 2010, fossil fuels were responsible for the release of 14.4 Gt of CO_2[1]. Fossil fuels are separated into three different components: oil, coal, and natural gas.

Oil is the most important source of energy worldwide, accounting for approximately 35% of primary energy consumption. Oil currently holds a monopoly on the transport market, representing over 95% of the energy requirements in this sector [3]. Transportation is a large contributor to CO_2 emissions as it relies almost exclusively on fossil fuels. This dependence on petroleum reserves has stimulated a worldwide search for alternative sources to petroleum based fuels [4]. Biomass is considered one of the most promising renewable energy resources that can be used as an alternate for fossil fuels.

Using biomass as a source of energy is attractive for a number of reasons. It reduces greenhouse gases; it can provide economic benefits to rural regions; and it can provide energy independence to countries without fossil fuel reserves [5]. Biomass energy reduces the amount of CO_2 by offsetting the use of fossil fuels. The burning of biomass releases carbon into the atmosphere that was recently absorbed by the plant matter which composes the biomass. This is in contrast to the burning of fossil fuels that contain carbon that was removed from the atmosphere millions of years ago. Biomass energy is used in a wide variety of methods [6]. Woods and fibers can be burned to provide heat, or digested to produce biogas. Sugars and starches can be fermented into alcohols, which can be used as a liquid fuel. Vegetable oils or animal fats can be transesterified into biodiesel or converted into other liquid fuels.

Biodiesel can be made from sources such as edible and inedible plant oils or animal fats. The oils and fats that are used in biodiesel production are broken down into two different categories: first generation and second generation [7]. First generation oils include readily available fats and oils that are produced for human consumption. These include soybean oil, canola oil, and beef tallow. Second generation oils are those that come from waste streams of first generation oils, such as waste cooking oil from the restaurant industry, or are produced specifically for biodiesel [7]. These include non-edible oils such as jatropha oil, algae oil, and used cooking oil. First generation oils are commodities that have already been processed to a food grade standard, which makes them easier to convert to biodiesel but also more expensive. Second generation oils are being produced strictly for conversion to biodiesel. Because they are not limited by laws regulating oils for human consumption, they can be produced cheaper. There are also other benefits such as the jatropha tree which can be grown on marginal land or algae that can produce more oil per acre than any crop can be exploited [8].

Biodiesel is a direct, cleaner, replacement for petrol diesel. There are a number of emissions from diesel vehicles that can cause health risks in urban areas, such as particulate matter, carbon monoxide, hydrocarbons, sulfur oxides, and nitrogen oxides. The use of biodiesel greatly reduces particulate matter, hydrocarbon, and carbon monoxide emissions compared to petrol diesel [9].

Vegetable oils and animal fats are made up of three fatty acid chains that are connected to a glycerol backbone. This chemical structure is called a triglyceride (TG). When the fatty acids are not attached to a backbone they are called free fatty acids (FFA). Hydrolysis of triglycerides, which is the process of splitting FFA off of the glycerol backbone, has been performed in industry for many years. FFA are used for the creation of soaps and surfactants, but recently processes have been developed to convert FFA into biofuels [10]. Triglycerides and FFA can also be converted into biodiesel through a transesterification reaction with methanol or ethanol [11]. This process splits the fatty acid chain off of the glycerol backbone and replaces it with an alcohol. For a reaction with methanol, the result is a fatty acid methyl ester (FAME), which is commonly known as biodiesel.

Triglycerides must be purified before they can be converted into biodiesel, as they contain water, gums, minerals, free fatty acids and other impurities that can impact the transesterification process. The most commonly used transesterification process is a base catalyzed process. This process is very sensitive to water and FFA impurities in the reaction [12]. A common purification step is to use an acid catalyst to esterify any FFA in the oil. Acid catalyzed esterification is not water sensitive, so this can be done before dehydrating the oil. The drawback to using an acid catalyst is that it takes more time to react than base catalysts do. For commercial production, homogeneous catalysts are used. These are catalysts that dissolve in the reaction mixture. The use of a homogeneous catalyst adds a neutralization and purifying step to the biodiesel process designed to remove the catalyst. One way of avoiding these extra steps is to use a solid catalyst that does not dissolve into the mixture. These catalysts are called heterogeneous catalysts.

Research is being conducted [13] to find a heterogeneous catalyst for the transesterification reaction that meets these three criteria:

1) Effective
2) Reusable
3) Low cost

A heterogeneous catalyst must be able to produce biodiesel that meets ASTM standard D6751 [14]. The standard states that there can be a maximum of 0.24%wt glycerol and 0.40%wt monoglycerides in the biodiesel. This equates to a molar conversion of 99.3%. This high conversion rate can be achieved by varying factors such as methanol concentration, temperature, catalyst density, and reaction time. A catalyst that can drive the reaction to completion with a low temperature and reaction time will reduce the overall costs for the reaction. The catalyst must have a reactor design that enables it to produce biodiesel that meets ASTM standard D6751. A heterogeneous catalyst that has a high reusability factor, or a low fowling factor, enables it to function for longer periods of time. This will decrease the amount of catalyst that is required and reduce the maintenance time required to

refresh the catalyst. The longer a catalyst maintains its effectiveness, the lower its per-use cost is. A heterogeneous catalyst must have a lower cost per use than the cost of a homogeneous catalyst and its neutralization agent to be cost effective.

There are also indirect savings to using a heterogeneous catalyst. Having a durable and reusable catalyst simplifies the process of creating biodiesel. It does this by eliminating the neutralization and purification steps. This simplification reduces the costs associated with these steps. None of the catalysts that have been evaluated in literature have met all three of these criteria [12–17]. Some of these catalysts are outlined in Table 4.

Sulfonated polyether ether ketone (SPEEK) is a polymer that was studied for its use in fuel cells [21]. It is used as a proton exchange membrane, but also has catalytic properties. These properties have not been evaluated in a biodiesel synthesis reaction.

Polyether ether ketone (PEEK) is sulfonated using concentrated sulphuric acid [22] or produced using presulfonated monomers [23]. The amount of sulfonated monomers in SPEEK is measured by a degree of sulphonation (DS). A DS of 0 does not contain any monomers that have been converted to SPEEK, while a DS of 1 is SPEEK with one Sulphur group on each monomer. When PEEK is sulfonated its strength is reduced [24]. Its strength is reduced even more when it is exposed to a solvent. This occurs because SPEEK becomes hygroscopic when its DS increases [25]. Despite the reduction in strength, tensile strength of SPEEK with a DS of 0.69 after being submerged in water is 19.5 MPa [24], which is equivalent to the strength of HDPE [26]. With an increase in DS, SPEEK will absorb water or, more importantly, methanol. The higher the DS, the more methanol it will absorb. At a DS of 0.4, SPEEK becomes soluble in boiling methanol. At a DS of 1, SPEEK becomes soluble in hot water [27]. SPEEK with a DS = 0.2-0.4 has the potential to have the catalytic activity and durability required to be used as a heterogeneous catalyst in transesterification reactions for the production of biodiesel.

Therefore, this research work proposes to determine the effectiveness of SPEEK as a catalyst for the production of biodiesel. To do so it first proposes to produce SPEEK and apply existing kinetic models found in the literature to the experimental results for the sulphonation of PEEK. The kinetic results will then be used to manufacture a solid catalyst with a DS between 0.2 and 0.4. This catalyst will be evaluated for its effectiveness for the transesterification of triglycerides.

Triacetin, a short-chain triglyceride, will be used as a representative triglyceride in studying the effectiveness of SPEEK as a catalyst for transesterification reactions. A baseline kinetic curve will be established for comparison using sulphuric acid as a homogeneous catalyst. SPEEK with a DS of 1.0 will then be used as a homogeneous catalyst to compare its effectiveness directly with sulphuric

acid. A solid heterogeneous SPEEK catalyst will then be evaluated in transesterification reactions and compared to the homogeneous catalysts. The durability of the catalyst will also be examined by using the same catalyst for multiple experiments to determine its effectiveness over time. This research will evaluate whether further research should be committed to using SPEEK as a catalyst for biodiesel production.

2 Literature Review

2.1 Biodiesel

Biodiesel is a direct substitute for petrol diesel [28]. As can be seen in Table 1, the density, viscosity, and cetane number are similar. Biodiesel has a higher cloud and pour point than diesel, which limits its use in cold weather. This can be overcome by mixing biodiesel with petrol diesel during the colder months of the year. Biodiesel also has no sulfur content, which eliminates the production of SOx when burning pure biodiesel [29].

Table 1: Properties of Biodiesel vs Diesel [29]

Specifications	Biodiesel	Diesel
Density (15 °C) (kg/m^3)	870–895	810–860
Viscosity (40 °C) (cSt)	3.5–5.5	2–3.5
Cetane number	45–65	40–55
Cold filter plugging point (°C)	−5 to 10	−25 to 0
Cloud point (°C)	−5 to 10	−20 to 0
Pour point (°C)	−15 to 10	−35 to 0
Lower heating value (MJ/kg)	36.5–38	42.5–44
Water content (mg/kg)	0–500	
Acid number (mg KOH/g)	0–0.60	
Ester content (% w/w)	>96	
Glycerin content (% w/w)	0–0.25	
Sulfur content (mg/kg)		15–500

Biodiesel is a common term for fatty acid methyl esters (FAME) that are derived from renewable sources [30]. These renewable sources are animal fats, vegetable oils and nonedible plant oils. They can be broken down into two different categories: first generation and second generation triglycerides [7].

A representation of the chemical structure of a typical triglyceride is shown in Figure 2. The molecule is made up of three fatty ester chains connected to a glycerol backbone. The ester chains on each molecule can be different, and the ratios of the ester chains are different for each type of oil [31]. Some commonly

used oils can be seen in Table 2 that show the ratio of the different fatty acids in each. This difference in fatty acid composition gives the feed stocks different properties, which in turn gives the biodiesel different properties. An example of this is the gel point for palm oil based biodiesel is higher than that of soybean based biodiesel [32].

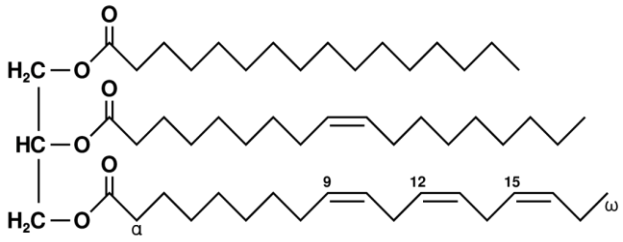

Figure 2: Example of a triglyceride

Table 2: Typical fatty acid composition from common oil sources [31]

Fatty acid	Chain Length: # of double bonds	Soybean	Cotton seed	Palm	Lard	Tallow	Coconut
Lauric	C12:0	0.1	0.1	0.1	0.1	0.1	46.5
Myristic	C14:0	0.1	0.7	1.0	1.4	2.8	19.2
Palmitic	C16:0	10.2	20.1	42.8	23.6	23.3	9.8
Stearic	C18:0	3.7	2.6	4.5	14.2	19.4	3.0
Oleic	C18:1	22.8	19.2	40.5	44.2	42.4	6.9
Linoleic	C18:2	53.7	55.2	10.1	10.7	2.9	2.2
Linolenic	C18:3	8.6	0.6	0.2	0.4	0.9	0.0

TG are reacted with methanol (MeOH) through a process called transesterification to produce FAME. The reaction happens in three steps as indicated in equations 2-4. The three reactions are commonly summarized into an overall reaction, which can be seen in Equation 1 [33]. In step one, TG reacts with MeOH to form a diglyceride (DG) and a FAME. The DG then reacts with another MeOH molecule to form a monoglyceride (MG) and a FAME. The MG then reacts with another MeOH molecule to form glycerol (Gly) and a FAME. Each of these reactions is reversible. FFA can be converted into FAME through a process called esterification [34]. The reaction consumes one methanol and one FFA molecule and produce one water and one FAME molecule.

$$TG + 3MeOH \rightleftharpoons Gly + 3FAME \quad (1)$$

$$TG + MeOH \rightleftharpoons DG + FAME \quad (2)$$

$$DG + MeOH \rightleftharpoons MG + FAME \quad (3)$$

$$MG + MeOH \rightleftharpoons Gly + FAME \quad (4)$$

The yield of the reaction can be calculated from the weight of the FAME present in the reaction mixture. This is done through the theoretical material balance of the reaction, as shown in equation 5 [35]. In this equation, W_{FAME} is the weight of the fatty acid methyl ester, and M_{FAME} is its molar mass. W_{oil} and M_{oil} are the weight and the molar mass of the oil triglycerides respectively. The molar mass for the FAME and the oil triglcyerides is an average molar mass based on the abundance of each FFA chain in the source oil.

$$\text{FAME } yield\ (\%) = \frac{\frac{W_{FAME}}{M_{FAME}}}{3\frac{W_{oil}}{M_{oil}}}\ x\ 100 \quad (5)$$

The yield of the reaction is important because in order to be used in a vehicle, biodiesel must meet ASTM standard D6751 that requires a molar reaction yield of at least 99.3% [14].

2.2 Solubility and Phase Equilibrium

Solubility of methanol in oil is a critical consideration in the transesterification reaction. Under standard temperature and pressure conditions, oil and water are not soluble and form two phases. When the reaction is conducted using a homogeneous catalyst, the reaction takes place either in the methanol phase or on the surface of the methanol phase [36]. This occurs because the polar catalysts favor the polar methanol phase over the non-polar triglyceride phase of the reaction. When using heterogeneous catalysts the solubility of methanol in the triglyceride phase is also important. The triglyceride phase makes up the bulk of the volume, which means that the heterogeneous catalyst will be in contact with the triglyceride phase more than the methanol phase. The solubility of methanol in oil/biodiesel is dependent on four main factors: temperature, degree of saturation of the oil, reaction completion, and catalyst [37].

The solubility of methanol in beef tallow is fairly low, however, methanol will dissolve more readily in FAME [38]. When the FAME content increases to 70% the TG/FAME and methanol phases become one homogeneous phase [39]. This has an accelerating effect on the reaction rate. The temperature of the reaction also

has a factor in the solubility of methanol in the oil phase [37]. The hotter the temperature, the more methanol will dissolve into the oil phase, It has also been found that the degree of saturation of the oil also has an effect on the solubility of methanol in oil [39]. The more double bonds on the FFA chains, the higher the methanol solubility is.

The by-product of the reaction, glycerol, is not soluble in the oil phase. It is however soluble in methanol [31]. So, in a transesterification with methanol and triglycerides as the reactants, there are two distinct phases. Methanol will transfer from one phase to another throughout the reaction's duration. Because of this, when determining the kinetics of the reaction, the mass transfer between phases has a large effect on how fast the reaction occurs. To solve this problem, triacetin has been used as a representative molecule for vegetable oil and animal fat [16].

2.3 Triacetin

Triacetin is a simple short chain triglyceride. It consists of three acetin molecules attached with a glycerol backbone, which can be seen in Figure 3. It has been used as a representative molecule in transesterification reactions when studying the kinetics of different catalysts [19].

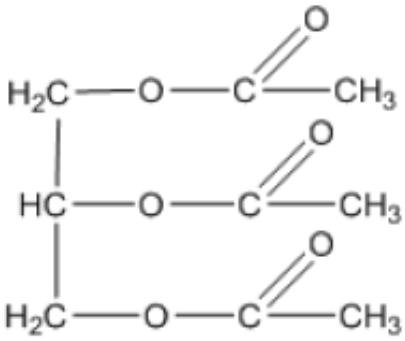

Figure 3: Triacetin molecule[19]

The benefits of using triacetin are that it is completely miscible in both methanol and glycerol [40], which eliminates the usual phase barrier and mass transfer effects influencing the reaction. This eliminates a complicating factor when looking at the kinetics of the reaction, which enables an easy comparison of the effects of different catalysts on the reaction rate of the biodiesel reaction. One of the downsides of using triacetin is the product of the reaction, methyl acetate, has a boiling point of 57°C, which is lower than the 65°C boiling point of methanol [41]. A typical methanolysis reaction would normally run at 60°C, which is higher than the boiling point of methyl acetate. This requires any reactions using triacetin to

occur at a lower temperature than one using a heavier triglyceride such as vegetable oil. Another downside to using triacetin is that the glycerol product remains in the same phase as the triglycerides, which increases its availability for the reverse reaction.

2.4 Transesterification Processes

There are four biodiesel production categories that have been studied [16], [42].

1) Catalytic reactions using an acid catalyst that is either homogeneous or heterogeneous;
2) Catalytic reactions using a base catalyst that is either homogeneous or heterogeneous;
3) Biologically using a lipase; and
4) Non-catalytic high temperature and pressure.

All four production categories have some steps that are in common. These steps can be broken down into three main stages [42]. An example of a typical biodiesel process can be seen in Figure 4.

1) Oil preparation;
2) Main reaction; and
3) Fuel conditioning.

In the oil preparation phase, the raw oils are cleaned and filtered to remove unwanted impurities and debris. Triglycerides come from a large variety of sources, and all of them have a variety of impurities that must be removed prior to transesterification. Virgin vegetable oil has water, gums, and FFA that must be removed [31]. Waste vegetable oil has particulates, water and FFA impurities [12]. Depending on the main reaction not all of these impurities need to be removed [43]. The preparation phase can be seen in Figure 4 as everything before the neutralized oil box.

The main reaction converts the oil to biodiesel. These are the four biodiesel production categories. They are represented in Figure 4 by the transesterification box. Each category would have slightly different processes in the preparation phases and fuel conditioning phases. These differences are discussed below.

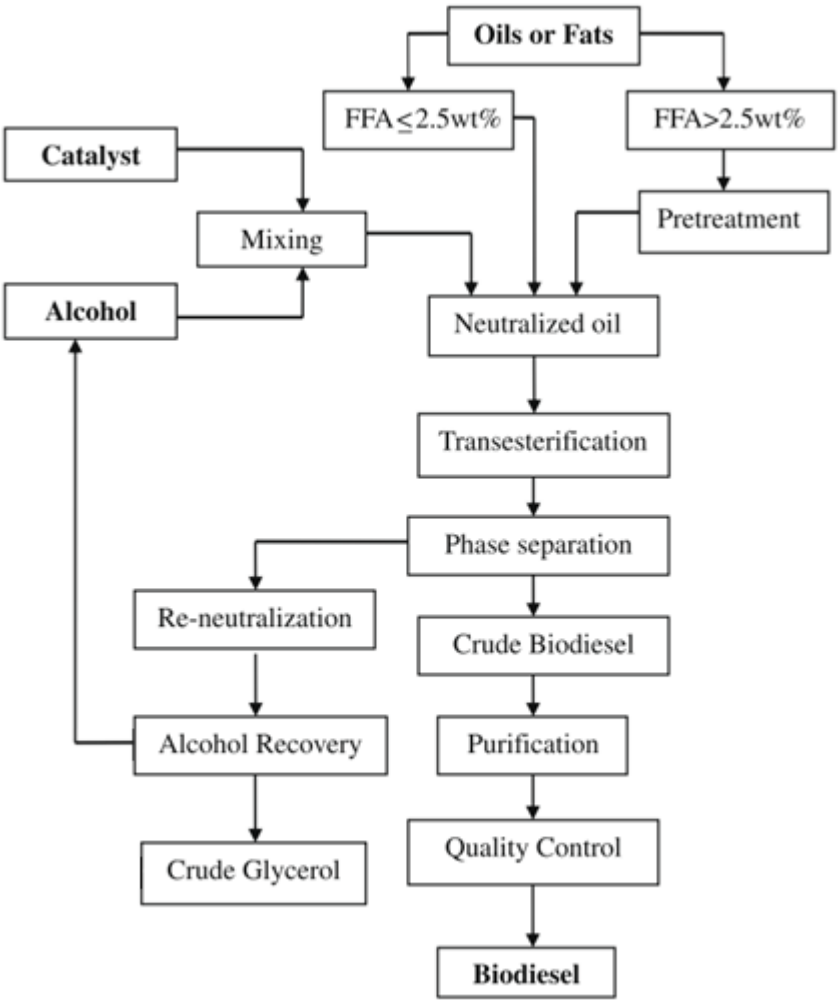

Figure 4: Flow chart for homogeneous alkali-catalyzed biodiesel production [42]

The fuel conditioning stage starts at the phase separation box. The biodiesel phase is separated from the methanol and glycerol phase. The biodiesel is then neutralized (if required) and cleaned of any impurities that were by-products of the main reaction. This is represented in Figure 4 by everything below the transesterification box.

Each of the four different methods have advantages and disadvantages for each of the three steps [44]. A summary of the advantages and disadvantages can be found in Table 3.

Base catalyzed reactions, with a homogeneous catalyst, is the predominant industrial method for the creation of biodiesel. A homogeneous base will reach 100% conversion faster than of any of the other three methods [45]. While using a co-solvent, Boocock et al. developed a production method that is able to reach 100% conversion in 7 minutes [46]. The reverse reaction rate with a base catalyst is significantly slower than the forward reaction, which allows for a small ratio of methanol to vegetable oil to be used [47]. The catalysts used for this type of reaction are often very inexpensive to purchase, such as NaOH or KOH. However, they cannot be reused or regenerated [48]. A base catalyst will react with water and FFA to produce a soap [49]. This soap has the dual effect of reducing the available catalyst for the reaction and creating emulsions that complicate the separation of glycerol from biodiesel in the fuel condition phase [50]. In order to use feedstocks with a high FFA or water content, additional processing in the oil preparation phase is required [51]. The base catalyst must be neutralized after the reaction and the by-products of the neutralization must then be washed out of the biodiesel. This adds extra processing time and costs [51].

Use of a heterogeneous base catalyzed reaction is still in the research stage [52]. The majority of research has been done using metal oxides such as SrO or CaO [53], [54]. The advantage of a basic heterogeneous catalyst, such as CaO, is its cost [34]. CaO can be obtained from natural sources, such as egg shells or mollusk shells or mineral sources such as limestone. The major drawback of the heterogeneous base catalyst is that it reacts with FFA to produce soaps [34]. The basic sites may be poisoned by strong adsorption of FFA and water on the surface sites [13]. Feedstocks with a high FFA must be pre-treated in order to reduce their FFA content. Without complete elimination of FFA in pretreatment, the catalyst is deactivated and soaps are formed.

Homogeneous acid catalysts do not have a sensitivity to dissolved water or FFA [55]. This simplifies the oil preparation stage of the process by removing the need to pretreat the source oils. Homogeneous acid catalysts do not form soaps when there is water present in the reaction [56]. This simplifies the separation of biodiesel from glycerol. Homogeneous acid catalysts must still be neutralized and washed out of the biodiesel. Despite being inexpensive to purchase, they are a reoccurring cost for the process. The drawback to homogeneous acid catalysis is that they react 4000 times slower than base catalysts [45]. The reverse reaction kinetics are faster, which requires a larger methanol to oil ratio be used in order to drive the reaction to completion [57].

Heterogeneous acid catalysts are still in the research stage [50]. There are many different materials that can function as this type of catalyst, which are broken down

Table 3: Summary of the advantages and disadvantages for different transesterification catalysts

Catalyst	Type	Advantages	Disadvantages
Acid Catalyst	Homogeneous	Limited feedstock pre-treatment required Converts FFA into biodiesel No reaction with water	High methanol ratio required Slow kinetics Neutralization required Purification of biodiesel required
	Heterogeneous	Neutralization of catalyst is not required Limited feedstock pre-treatment required Converts FFA into biodiesel No reaction with water Limited biodiesel purification	High methanol ratio required Slow kinetics Catalyst costs and deactivation
Base Catalyst	Homogeneous	Fast kinetics Can use a low methanol ratio	Feedstock pre-treatment required Neutralization required Purification of biodiesel required FFA reacts to form soaps Water reacts to form soaps
	Heterogeneous	Neutralization of catalyst is not required Fast kinetics Can use a low methanol ratio	Feedstock pre-treatment required Purification of biodiesel required FFA reacts to form soaps Water reacts to form soaps Catalyst costs and deactivation
Biological	Lipase	Limited biodiesel purification Converts FFA into biodiesel Low energy inputs	Slow kinetics Catalyst costs and deactivation Water reduces conversion rate Methanol ratio
No Catalyst	High Temp	Fast kinetics Neutralization of catalyst is not required Limited feedstock pre-treatment required Converts FFA into biodiesel No reaction with water Limited biodiesel purification	High energy costs High setup costs High methanol ratio required

in Table 4. The benefits of using a heterogeneous acid catalyst is that it will perform both alcoholysis on FFAs as well as transesterification on TGs without a soap byproduct [34]. The use of a heterogeneous catalyst also eliminates the requirement for neutralization, which reduces the number of steps required to purify the final product [40]. The drawback of using a heterogeneous acid catalyst is the low activity level of the catalyst as well as catalyst deactivation [50]. An acid catalyst can be up to 4000 times slower than a base catalyst under the same reaction conditions [45]. This reduces a plant's production and is a large financial deterrent to using an acid catalyst. Deactivation of catalysts can occur from mechanical damage, or blockage of the catalytic sites by adsorbed intermediates and product species [58].

Lipase catalysts are "immobilized enzymes that are physically confined or localized in a certain defined region of space with retention of their catalytic activities, and which can be used repeatedly and continuously" [59]. They are generally immobilized on acrylic resin, textile membranes, polypropylene, celite and diatomaceous earth [60]. They have excellent catalytic activity and stability in non-aqueous media, which facilitate the esterification and transesterification process during biodiesel production [60]. They are a heterogeneous catalyst that does not require neutralization in the fuel conditioning stage of the process. Lipase catalysts can perform alcoholysis of FFA, but are sensitive to the concentration of water in the reaction. Reduction in catalyst effectiveness occurs when the weight percentage of water goes beyond 8% of the weight of catalyst used [61]. Another disadvantage to using a lipase catalyst is that the catalyst is expensive and not durable [59]. The bonds holding the enzymes in place are weak and the enzymes are often dislodged. Lipase catalysts have activities that are similar to the activities of acid catalysts [60]. Lipase catalyzed reactions are sensitive to methanol concentrations in the reaction mixture. Having a methanol:oil ratio greater than 1:1 deactivates the catalyst which severely reduces the conversion. At a mole ratio of 6:1 the conversion rate drops from 95% to less than 5% [62].

A non-catalyzed reaction of TG into biodiesel occurs at high temperatures (200-400°C) and pressures (up to 10MPa) [63]. Conversion will reach 75% after three hours at 200°C with a methanol:oil molar ratio of 42:1, and at 400°C conversion will reach over 95% in less than 2 minutes [63]. The critical point of methanol is 239°C and 8.09 MPa [63]. Once the methanol enters its critical state, the reaction goes from 2 phases to 1 phase. The reaction occurs much faster in 1 phase [12]. Because no catalyst is used, the fuel conditioning phase is simplified. The process is not sensitive to dissolved water or FFA [64]. One of the drawbacks is that the kinetics of the reverse reaction are also increased, which means that a high methanol to oil ratio is required to obtain complete conversions[65]. Another drawback of this process is the high cost of setup. High pressure equipment is required, including pumps and heaters, which also makes it a very energy intensive process [66].

2.5 Heterogeneous Acid Catalysts

A lot of research has gone into finding new catalysts that will improve the economic viability of the transesterification reaction process. One of the most prominent categories is heterogeneous acid catalysts [16][19].

The main benefit of a heterogeneous catalyst over a homogeneous catalyst is that the catalyst is easier to separate from the reaction mixture [18]. This separation is done without the need to neutralize the catalyst. This enables it to be reused, which cuts down on the operating costs, specifically, those associated with continually buying catalyst and the process of neutralizing it [58]. A reusable catalyst will have a higher up front cost, but will reduce the total costs of catalysts over time [13]. Having a catalyst that is easily separated out also reduces the amount of washing that the biodiesel needs to undergo to meet international standards [54]. The reduction in processing steps associated with using a heterogeneous acid catalyst can be seen in Figure 5. This can be contrasted with the flow diagram in Figure 4. One of the key difference between the two processes is that the catalyst remains fixed in the transesterification reactor.

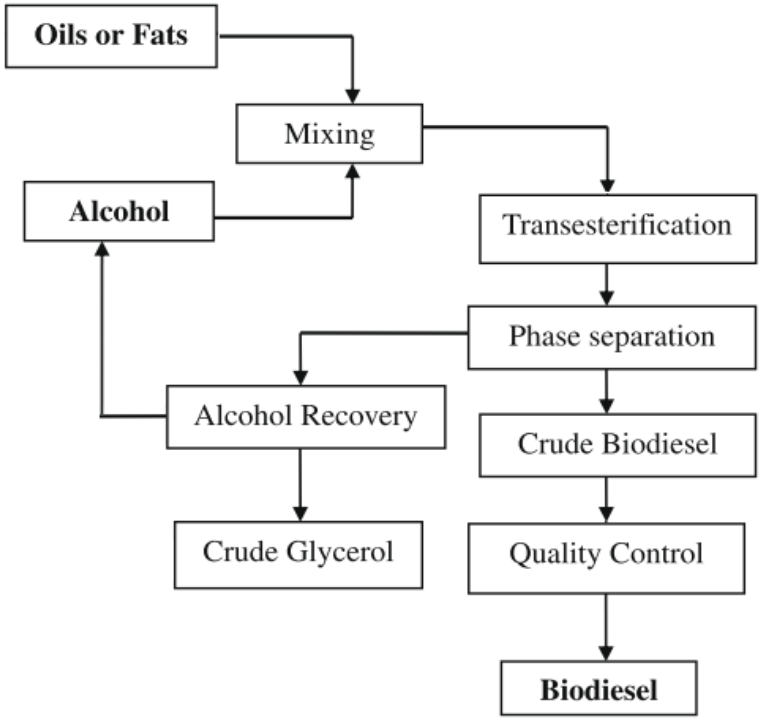

Figure 5: Process diagram for a heterogeneous acid catalyst used to transesterify triglycerides into biodiesel.

The use of a heterogeneous acid catalyst also simplifies the oil preparation phase. The catalyst's insensitivity to water or FFA enables a wide range of feedstocks to be used with little to no pre-processing [31]. This simplification in processing steps reduces the cost and footprint of a biodiesel processing facility. The downside to heterogeneous catalysts is the lower reaction rate associated with them [67]. Due to limited surface area, it is impossible for the same amount of catalyst to react as fast as a homogeneous catalyst [58].

There has been a significant amount of research done on heterogeneous acid catalysts for the biodiesel reaction. Su F. et al. [13] categorized the research and examined the effectiveness of the different groups of catalysts. A summary of their work can be seen in Table 4.

Table 4: Groups of heterogeneous acid catalysts and their effectiveness [13]

Group	Name	Examples	Reusability	Activity
1	Sulfated metal oxides	SO_4^{2-}/ZrO_2, SO_4^{2-}/Ta_2O_5, or SO_4^{2-}/Nb_2O_5	Medium	High
2	Sulfonic ion-exchange resin	Amberlyst, Nafion, Purolite, or EBD	Low	High
3	Sulfonic acid modified mesoporous silica	SBA and MCM series of inorganic silica or periodic mesoporous organosilica	Medium	Medium
4	Sulfonated carbon-based catalysts	Sulfonated D-glucose, sucrose, or cellulouse.	High	High
5	Heteropolyacids and supported Heteropolyacids	Early transition metals (V, Nb, Mo, Ta, or W) and oxygen anion clusters.	High	Medium
6	H-form zeolites	H-ZSM-5, H-MOR, H-BETA, or H-USY	Not studied	Poor
7	Acidic Ionic Liquids and immobilized Ionic Liquids	PDVB-$[SO_3H-(CH_2)_3VPy]HSO_4$, or [MOIm]-HSO_4@SBA-15-Pr-SO_3H	High	High

Category 4, sulfonated carbon based catalysts, shows a lot of promise as a biodiesel catalyst. Due to the addition of SO_3H groups, the catalysts become hydrophilic [13]. These materials can incorporate large amounts of hydrophilic molecules, including methanol, into the carbon bulk, which makes them readily available for reaction [68]. This gives rise to high catalytic performance despite the small

surface area of the materials [68]. A sulphonated cellulose powder is 60% as active as H_2SO_4 under the same reaction conditions [13]. Its activity is higher than conventional solid acids such as silica-supported Nafion (Nafion SAC-13), Amberlyst-15, and Nafion NR50 [13].

It has been shown that a sulfonated D-glucose catalyst was stable after fifty cycles of re-use [13]. This is more effective then commonly researched catalysts such as Nafion NR50 or Amberlyst-15 [16].

2.6 Transesterification Kinetics

This thesis looked at using Sulphonated Poly(Ether Ether Ketone) as a catalyst for the transesterification reaction. It has not yet been investigated as a catalyst for the production of biodiesel, but it falls into category 4 of the heterogeneous acid catalysts listed in Table 4.

The kinetics for the transesterification reaction are complicated. There are three reversible reactions that occur consecutively and in most cases when reacting with methanol, a phase boundary that slows the reaction down. [69] A chart of conversion as a function of time forms an S curve. The reaction is slow to start off, then reacts rapidly and then tapers off at the end. [69] For reactions with a molar ratio of methanol to oil of 30:1 the reaction follows pseudo-first-order kinetics, [31] but reactions with a 6:1 ratio follow second-order kinetics. [70]

The transesterification reaction follows a nucleophilic substitution by addition-elimination mechanism, and the kinetics of this mechanism are known to be second order. [71] The rate limiting step for this mechanism is the nucleophilic attack. This matches what literature has found. The reaction becomes pseudo-first order, with respect to the concentration of triglycerides, when the methanol concentration is much higher than the concentration of triglyceride in the reaction mixture.

Transesterification on a solid catalyst adds another complication factor to the kinetic rate. The ad/desorption of triglycerides and methanol onto the surface of the catalyst must be factored in. The Eley-Rideal Model has been found to best describe the transesterification kinetic rate on a solid catalyst. [72] When using a synthesized ion exchange resin as a catalyst, the rate determining step was determined to be the reaction on the surface of the catalyst. [72] This finding has been confirmed to hold true for the solid acid catalyst Nafion® SAC-13. [40]

2.7 Sulphonated Poly(Ether Ether Ketone)

PEEK is a semi-crystalline thermoplastic that can be used at high temperatures, has high strength, and excellent chemical resistance [73]. A summary of its properties can be seen in Table 5.

Its repeat units are made up of 3 aromatic rings connected by ether or carbonyl linkages [24]. A diagram of a repeat unit can be seen in Figure 6. The only thing that dissolves PEEK at temperatures below its melting point are strong acids [74], [75]. When dissolved in concentrated sulphuric acid, PEEK will react with the acid creating SPEEK. The chemical equation can be seen in Equation 6. it was found that the reaction was not reversible [76]. When sulfonated, an $-SO_3H$ group is attached to one of the aromatic rings, as can be seen in Figure 7. The carbonyl group in the monomer deactivates the two rings adjacent to it, leaving only the ring bonded with oxygen available for reaction. This ring has four sites on it that are equally favoured for sulphonation [77].

Table 5: Physical properties of PEEK and SPEEK under different conditions [24], [73].

Physical Properties			
Moisture Conditions	Relative Humidity = 30%		In Water
DS	0	0.63	0.63
Thermal Stability (°C)	580	330	--
Modulus (MPa)	3034	2404	716
Yield Stress (MPa)	--	62	15.1
Yield Strain (%)	--	5	3
Break Stress (MPa)	94.2	51.5	16.6
Break Strain (%)	6	50	60
Water uptake (wt%)	0	--	22.1

$$PEEK + H_2SO_4 \rightharpoonup SPEEK + H_2O \quad (6)$$

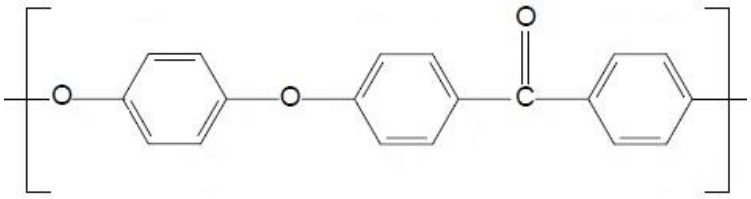

Figure 6: PEEK Monomer[78]

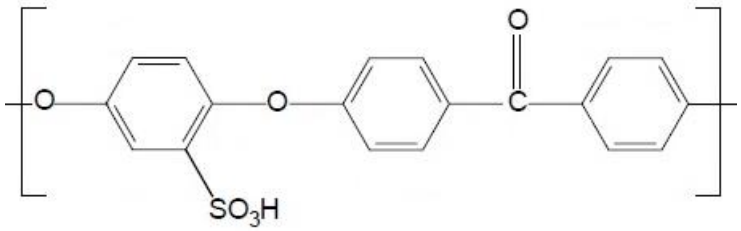

Figure 7: SPEEK Monomer[78]

Research into SPEEK began in 1985 with the publication of two papers by Bishop et al [74], [77]. The sulphonation reaction is an electrophilic substitution reaction where the sulfonic groups are introduced to the polymer chain. The carbonyl group deactivates the aromatic rings on either side of it leaving only one aromatic site per monomer for the reaction to occur [74]. This enables a degree of sulphonation (DS) to be established, with 1 being all repeat units having an SO_3H attached and 0 being no sulphonation has occurred. The DS can be controlled by reaction time, acid concentration and temperature [22], [74], [77], [79].

It was discovered that PEEK gets less soluble in sulphuric acid as the concentration of the acid decreases [74]. This can be seen in Table 6.

Table 6: Solubility of PEEK at 25°C. Reproduced from [74]

Solvent	Solubility
94.9% H_2SO_4	complete
89.9% H_2SO_4	nearly complete
84.8% H_2SO_4	partial
79.6% H_2SO_4	negligible
CH_3SO_3H	complete
CF_3CO_2H	negligible

There has also been some investigation of the solubility of SPEEK in different solvents [77]. The DS has a large impact on the solubility of a sample of SPEEK. A summary of this can be seen in Table 7. As the SPEEK becomes more sulfonated it becomes more soluble in polar solvents such as methanol or water. SPEEK will absorb and hold these solvents (whereas PEEK will not) [25]. The higher the degree of sulphonation, the more solvent it will hold. At a DS = 1.0 SPEEK is soluble in warm water. In cold water it will partially dissolve and form a stable emulsion whereas, at a DS < 0.7 SPEEK will not dissolve in water [80].

Table 7: Solubility of SPEEK at room temperature. Reproduced from [77]

Solvent	Degree of sulphonation		
	0.72	0.32	0.04
Benzyl Alcohol	Soluble	Swollen	Insoluble
Dimethyl acetamide	Soluble	Swollen	Insoluble
Dimethyl formamide	Soluble	Swollen	Insoluble
Dimethyl sulphozide	Soluble	Swollen	Insoluble
m-Cresol	Soluble	Swollen	Insoluble
Phenol	Soluble	Swollen	Insoluble
Ethylene glycol	Soluble	Insoluble	Insoluble
Formic acid	Soluble	Insoluble	Insoluble
Pyridine	Soluble	Insoluble	Insoluble
Glycerine	Swollen	Insoluble	Insoluble
Methanol	Swollen	Insoluble	Insoluble
Propylene glycol	Swollen	Insoluble	Insoluble
Tetrahydrofuran	Swollen	Insoluble	Insoluble
Dichloroacetic acid	Swollen	Insoluble	Insoluble
1-Butanol	Insoluble	Insoluble	Insoluble
1-Propanol	Insoluble	Insoluble	Insoluble
Acetic acid	Insoluble	Insoluble	Insoluble
Acetone	Insoluble	Insoluble	Insoluble
Chlorobenzene	Insoluble	Insoluble	Insoluble
Chloroform	Insoluble	Insoluble	Insoluble
Ethanol	Insoluble	Insoluble	Insoluble
Toluene	Insoluble	Insoluble	Insoluble
Trifluoracetic acid	Insoluble	Insoluble	Insoluble

The sulphonation of PEEK changes its physical properties [24], [73]. A summary of these changes can be seen in Table 5. PEEK is thermally stable up to 580ºC, whereas SPEEK with a DS of 0.72 starts to thermally degrade at 330ºC [73]. SPEEK starts to degrade at this lower temperature because the SO_3H group decomposes at a lower temperature than the polymer. There is a second decomposition point at 515°C where the PEEK backbone begins to degrade [73]. The tensile mechanical properties are also lowered with an increase in the degree

of sulphonation [24]. Pure PEEK is semi-crystalline which leads it to be brittle, while SPEEK remains amorphous. This allows SPEEK to strain before it breaks. The greater the degree of sulphonation, the more a sample will strain before it breaks. Pure PEEK has a tensile strength of over 90 MPa [24], whereas SPEEK has a tensile strength of closer to 50 MPa [24]. When saturated with water, SPEEK loses a lot of its strength. SPEEK absorbs water which acts as a plasticizer and allows the polymers to slip around each other easily. The tensile modulus for a SPEEK sample with a DS of 0.63 was reduced by 70% after being exposed to water [24]. Samples with higher degrees of sulphonation had a greater reduction in tensile modulus. Increasing the temperature caused a further decrease in strength due to the increased amount of water absorbed by the SPEEK.

2.8 SPEEK Kinetics

The kinetics of the PEEK to SPEEK reaction were first examined by Shibuya and Porter [22]. Their work was based off of Cerfontains work on sulfonating aromatic rings [81]. Aromatics (Ar) react with sulphuric acid in a first order reaction [81]. The kinetics equation can be seen in equation 7. For this reaction an excess of sulfuric acid is used, which allows the sulfuric acid and water concentrations to be assumed as a constant. This sulfuric acid constant (Cs) is shown in equation 8. x and y in equation 8 are the reaction orders for the concentration of sulphuric acid and water respectively. Putting equation 8 into equation 7 simplifies it to equation 9. Shibuya combined Cs into the first order rate constant for all of his calculations. This is represented by equation 10.

$$-\frac{d[Ar]}{dt} = k\,[Ar]\,\frac{[H_2SO_4]^x}{[H_2O]^y} \tag{7}$$

$$\frac{[H_2SO_4]^x}{[H_2O]^y} = C_s \tag{8}$$

$$-\frac{d[Ar]}{dt} = k\,C_s\,[Ar] \tag{9}$$

$$kC_s = k_1 \tag{10}$$

Daoust et al. proved that using a lower concentration of sulfuric acid will result in a slower reaction [82] but did not go further to determine the order of the sulphuric acid and water concentrations in the reaction. They determined that an increase in sulphuric acid concentration from 95.9% to 98.6% increased the reaction rate by 14 times. No explanation was given for this change in reaction rate.

Starting with equation 9, the aromatic concentration can be shown as a function of concentration (C), with the initial concentration as C_o which can be combined with equation 10 to give equation 11. This kinetic reaction can be integrated as a function of t and C to get equation 12. Equation 13 shows the relationship between the concentration and the initial concentration, where X represents the degree of

sulphonation. Combining equation 12 and 13 gives equation 14, the integrated rate law for a first order reaction. This is used for comparing conversion rates as a function of time [27].

$$-\frac{dC}{dt} = k_1\, C \tag{11}$$

$$-Ln\left(\frac{C}{C_o}\right) = k_1 t \tag{12}$$

$$C = C_o(1 - X) \tag{13}$$

$$-Ln(1 - X) = k_1 t \tag{14}$$

Shibuya determined that there was a "deflating effect" on the first order reaction kinetics, or in other terms, a slowing of the reaction rate as the reaction progressed. He assumed that since some of the aromatic sulphonation reactions were reversible, this must be what is slowing the reaction down. He created a kinetic model for a reversible reaction that fit his data, which was later proved false by Daoust [82]. Daoust tested for a reverse reaction and found none, whereas Shibuya et al. assumed there was one, but did not verify. Daoust then proved that the deflating effect was caused by hindrance from previously reacted monomers [76]. He proved what caused the deflating effect, but did not come up with a definite equation for the kinetics of the SPEEK reaction.

Shibuya also calculated the activation energy (E_a) of the reaction. [22] This is done using the Arrhenius equation, Equation 15. This equation can also be expressed as equation 16 where LnK vs 1/T can be plotted and the slope and intercept can be used to determine the E_a and k_o.

$$k = k_o\, e^{\frac{-Ea}{RT}} \tag{15}$$

$$\ln k = \ln k_o - \frac{Ea}{RT} \tag{16}$$

Sulphonation of aromatic hydrocarbons, in sulfuric acid, have a reported activation energy in the range of 75-96kJ/mol [79–81]. Shibuya et al. calculated an activation energy of 85.4 kJ/mol. [22] Huang et al. also calculated the E_a for the reaction but got a value of 78.7 kJ/mol with a K_o of $1.3*10^{11}$. These findings still fall within the range listed above, but are very different compared to that reported by Sibuya et al. A more detailed look at the E_a is required after taking the effect of the concentration of sulphuric acid and water out of the reaction constant. This will allow for an E_a and K_o that can be used independent from the concentration of acid used in the reaction.

2.9 Proposed Research

The aim of this thesis is to determine if SPEEK can be used as an effective catalyst, can be durable, and reusable. This work was done in two phases:

1) Verified the rate of reaction for the sulphonation of PEEK and produce SPEEK to be used as a catalyst.
2) Determined the effectiveness of the SPEEK catalyst in transesterification reactions and compared against a sulphuric acid catalyst.

2.9.1 Phase One

The aim of phase one was to produce a SPEEK catalyst with a high DS that could be studied in homogeneous catalyzed transesterification reaction and a SPEEK catalyst with a lower DS that could be used in heterogeneous catalyzed transesterification reactions. The approach for the latter is to partially sulfonate PEEK pellets as to obtain a catalyst with a layer of SPEEK on a PEEK core. The concept is shown in Figure 8. Phase one of the research can be broken down into three steps:

1) Kinetic rates
2) Solubility rates
3) Catalyst design

The first step was to verify the published kinetics for sulphuric acid in the sulphonation of PEEK. This is required to build a model that can accurately determine the DS of a SPEEK sample given the reaction variables of temperature, time, and sulphuric acid concentration.

In the second step, the rate of solvation of PEEK into sulphuric acid was measured. This rate also varies with temperature and sulphuric acid concentration. This rate was balanced with the kinetic rate from step one to have an effective surface reaction without completely dissolving the PEEK core.

Step three involved determining the ideal conditions to effect a surface reaction on a PEEK pellet without dissolving the core of the pellet.

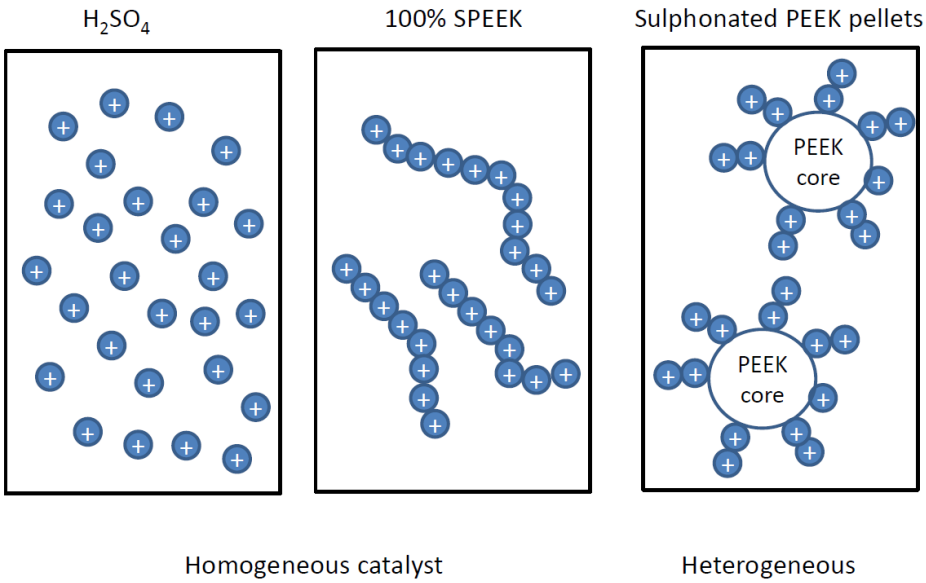

Figure 8: Conceptual representation of the catalysts proposed to be used in the transesterification experimentation.

2.9.2 Phase Two

In phase two, the SPEEK catalysts that were produced in phase one were examined to determine their effectiveness as a catalyst in a transesterification reaction. Phase two was broken down into four steps:

1) Verify the kinetics with a homogeneous sulphuric acid catalyst
2) Determine the kinetics with a homogeneous SPEEK catalyst
3) Determine the kinetics with a heterogeneous SPEEK catalyst
4) Determine the longevity of the SPEEK catalyst

The first step was to set a baseline kinetic rate using sulphuric acid. Triacetin was used as the triglyceride for the experiment. The reaction was run in a batch reactor at 50°C to ensure that the methyl acetate produced remained in solution. This baseline was used as a comparison for the next two steps.

The second step was to verify that SPEEK effectively catalyzed the transesterification reaction. SPEEK with a DS of 1.0 was used as a homogeneous catalyst which completely dissolves in methanol and triacetin.

The third step was to determine the activity of a heterogeneous SPEEK catalyst.

In the fourth step, the heterogeneous catalyst of step three was used for multiple transesterifications and the conversion rates evaluated to determine if there is any loss in catalytic activity.

In the next chapter, the methodology for the above experiments is presented in detail.

3 Experimental

In this chapter there are 4 major subdivisions outlining the procedures for the experiments. First the materials, chemicals and equipment are outlined, then phase one and two of the experimentation. In phase one the procedures for PEEK sulphonation and catalyst formation are listed, as well as the sampling and sample evaluation procedure. In phase two the procedures for using the catalysts in transesterification reactions are listed. The sampling techniques and examination methods are also shown.

3.1 Materials and Chemicals

3.1.1 Reagents

Two batches of polymers were used. The first was 2mm PEEK tubing produced by Upchurch Scientific Products. The second was PEEK pellets in the shape of cylinders measuring 2mm by 3mm. It was purchased from Victrex and had an average molecular weight of 105,000 g/mol.

18M H_2SO_4 was used as the acid for all experimentation. It was diluted to lower concentrations using deionized water when required. It was purchased from Fisher Scientific Limited.

99% Triacetin and methanol were both purchased from Fisher Scientific. They were both used in the transesterification reaction. DMSO – d_6 was purchased from CDN Isotopes and was used for ^{1}HNMR analysis. It contained 99.9% D and had an additive of 0.05% TMS. It was from lot AB-333.

3.2 Equipment

3.2.1 1H NMR

Spectra of samples were taken using a DMSO-d_6 solvent on a Bruker Ascend 400 Mhz NMR. The software used to render the spectra was Bruker TopSpin 3.5 pl 5.

3.2.2 Scanning electron microscope (SEM) and Energy dispersive X–ray analysis (EDX)

The SEM used was a FEI Quanta 250FEG. It used an LFD detector and ran at a pressure of 200 Pa. The EDX used for pellet characterization was an EDAX octane elite plus detector. It was used at 20 kV and had a takeoff angle of 34.2°.

3.2.3 Other lab equipment

The constant temperature bath used was a Corning hotplate/stirrer model number PC-420 with temperature controller 400085 lot 001857. The digital thermometer

used to ensure the accuracy of the temperature controller was a Traceable® Thermometer with a range of -50 to 150°C. The oven used for dehydrating samples was a Binder ED400. The centrifuge used was a Fisher Scientific, centrific model 228. It has a fixed speed of 3300 rpm.

3.3 Phase 1 - PEEK Sulphonation

When PEEK is sulfonated it follows the reaction in equation 17.

$$PEEK + H_2SO_4 \rightleftharpoons SPEEK + H_2O \quad (17)$$

3.3.1 Rate of solvation

When PEEK is added to concentrated sulphuric acid it dissolves [75]. Factors that affect how PEEK dissolves into sulphuric acid are temperature, mixing speed, sulphuric acid concentration, and SPEEK conversion. All four factors affect the rate the same way: the factor and the rate are directly proportional. To produce a catalyst with a PEEK core and a SPEEK shell, the rate of solvation must be minimized so that the surface reacts before the sample completely dissolves. So to limit the solvation, sulphonation of the PEEK pellets was performed in stagnant sulphuric acid.

An experiment was designed to determine the rate of solvation in different acid concentrations. The concentrations used for this experiment can be seen in Table 8. The experiment was run at 25°C for 25 hours. The PEEK samples were made up of 2mm PEEK tubing that was cut to lengths of 40 mm. Each sample used 7 ml of sulphuric acid. The samples were visually monitored for the duration of the experiment to determine how quickly the PEEK was dissolving.

A contributing factor that affects the solvation rate of PEEK into sulphuric acid is the reaction of PEEK into SPEEK. There are two main effects from this. The first is the creation of SPEEK, which is more soluble than PEEK. The second is the usage of sulphuric acid and the liberation of water at the reaction site. This has the effect of diluting the sulphuric acid near the PEEK sample, which reduces the solvation rate.

Table 8: Experiment to determine the rate of solvation of PEEK in varying concentrations of sulphuric acid

Sample	Sulphuric Acid Concentration (% wt)
1	94.0
2	92.5
3	90.0
4	87.5
5	85.0

3.3.2 Kinetic rates

The aim of this section is to compile data to calculate the Activation Energy (Ea) and the kinetic constant (k_o) from equation 16 and to compare the results with those found in the literature [78].

The reactions were carried out in a batch reactor configuration as shown in Figure 9. A constant temperature bath was used to maintain the temperature inside the reaction vessel at the temperature designated in Table 9. The bath was set on the thermostatically controlled heater which kept the temperature of the bath constant. A magnetic stirrer was placed in the bath to keep the temperature profile inside the bath consistent. This set up allowed for a constant temperature inside the reaction vessel without the need to maintain a thermometer probe in concentrated sulphuric acid. The reaction vessel was a three necked round bottom flask with a Teflon coated magnetic stirrer. A thermometer was used periodically to ensure that the temperature inside the reaction vessel matched that of the constant temperature bath.

For the sulphonation, the sulphuric acid was pre-heated to the designated temperature. PEEK was added to the sulphuric acid to obtain a density of 0.050 g of PEEK per cm^3 of sulphuric acid. Once the PEEK was added to the sulphuric acid, it took approximately 1 hour for it to fully dissolve. Occasionally PEEK would stick to the walls of the reaction vessel. A glass rod was used to mechanically remove and return the PEEK to mixing, which greatly increased the rate of solvation. The solution was constantly stirred for the duration of the reaction.

Table 9: Sulphonation of PEEK reaction kinetics experiments.

Reactions	Temperature (°C +/- 2°C)	$[H_2SO_4]$ (% mass)
SPEEK1	70	94
SPEEK2	60	94
SPEEK3	40	94
SPEEK4	60	94

Based on the data from literature [78], an approximate reaction time of 24 hours was used. Solution samples were taken every two hours for the first 8 hours then a final sample was taken at the 24 hour mark.

Due to the solubility issues involved with SPEEK with a DS of 1.0, a great deal of care was required to obtain accurate results. 300 ml of 10°C water was added to the samples to end the reaction and dilute the sulphuric acid. A new technique was developed using the density difference between the sulphuric acid solution and water. The sample solution was slowly run down the side of the beaker, using an eye dropper, into the water. This allowed the SPEEK to precipitate out of the reaction solution and bind to itself as the sulphuric acid dissolved into the water. Part of the sample dissolved into the water forming a milky solution, but the majority of the sample formed a solid film. This film was then washed with 10°C water to remove the remaining sulphuric acid. After the sulphuric acid was removed, the sample was then dried in an oven at 80°C for 24 hours and washed and dried again. This was repeated until the wash water obtained a stable pH.

After the planned reaction time was completed, the reaction was left to react for another 24 hours which brought the DS up to 1.0. Due to the low temperature of reaction the SPEEK3 trial was not used to produce SPEEK with a DS of 1.0. This SPEEK was used to determine the effectiveness of homogeneous SPEEK as a catalyst for the transesterification reaction.

It was prepared by slowly running 10°C distilled water through the washing mixture for 4 hours. The SPEEK was then dried at room temperature for 7 days and washed again. It was then oven dried at 80°C until it formed a film, the film was washed with 10°C distilled water until the pH of the water stabilized. The SPEEK was then dried in an oven at 80°C for 24 hours, and weighed.

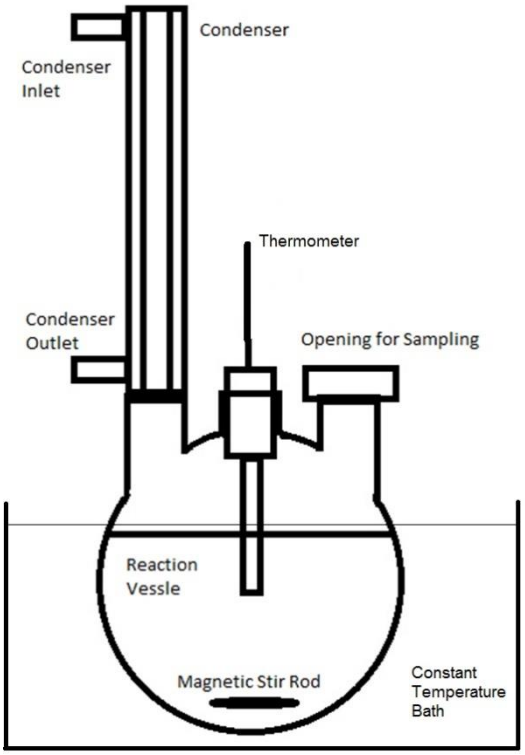

Figure 9: Reaction vessel for examining the kinetics of the SPEEK reaction

3.3.3 Catalyst formation

The SPEEK catalyst was produced in pellet form. The pellets were formed so that they had a core of PEEK, with an outside coating of SPEEK. These catalyst pellets were all formed using one standardized method.

Catalyst pellets were produced in 10ml test tubes, which contained 7 ml of 18M H_2SO_4. 0.17 g of PEEK (which consisted of 10 PEEK pellets measuring 2mm x 3mm) were mixed into to the sulphuric acid. The test tubes were 10mm in diameter, which resulted in a catalyst pellet that was roughly a cylinder of 10mm in diameter by 10mm deep. The PEEK was fully wetted to ensure that a reaction would occur over their full surface area. The PEEK partially dissolved into the sulphuric acid, but because of the difference in density, the majority of the PEEK floated at the top of the test tube. This formed a viscus disc of partially dissolved PEEK. The individual PEEK pellets clumped together to form a solid core, while the partially dissolved PEEK surrounded them and linked them together.

The samples were held at 25°C for 4 hours to allow the disc to form on the top of the sulphuric acid. They were then placed in an oven set at 80°C and atmospheric pressure for two hours. The test tubes were then removed from the oven and the

SPEEK discs were flipped over to expose the top of the disc to the bulk of the sulphuric acid. The test tubes were then slowly cooled to 25°C and left to react for another 18 hours. This ensured conversion on both sides of the disc.

To end the reaction, the catalyst pellets were removed from the test tubes and they were placed in a bath of 10°C distilled water. The bath water was constantly exchanged until the water running out of it measured a pH of 6-7. The catalyst pellets were left in a water bath for an additional 24 hours with periodic water exchanges. This ensured that any remaining sulphuric acid was able to escape the catalyst pellets.

SPEEK on the outside of the catalyst pellets has a maximum DS of 1.0. In order to obtain a catalyst with a DS between 0.2 and 0.4, the outer layers of the catalyst were removed. To do this, the solubility of SPEEK in different solvents was exploited. The pellets were put through two different wash stages.

The first stage was a 100°C boiling water wash. They were washed for 1 hour. The water was then changed and they were then washed in boiling water for another hour. This procedure was designed to dissolve the outer shell of the pellets and remove any remaining sulphuric acid. It also removed any catalyst that was weakly attached to the pellets.

The next stage was to wash the catalyst pellets in 65°C boiling methanol. According to Table 7, methanol will dissolve SPEEK with a DS over 0.7. The catalyst was boiled for 1 hour, then the methanol was exchanged and it was boiled for another hour. It was washed three times in this manner.

The catalyst was dried in an oven at 80°C for 24 hours then weighed. It was stored in a sealed container with desiccants to prevent atmospheric moisture from being absorbed.

3.3.4 Degree of Sulphonation

Two methods for determining the DS of a sample were used. For the PEEK sulphonation experiments an NMR spectra was utilized. For the catalyst pellets an EDX spectra was used.

When using the NMR spectra, DMSO-d_6 was used as the deuterated solvent. The solvent dissolved SPEEK with a DS of 0.4 or higher.

To prepare a sample, 0.01 g of SPEEK was placed in a NMR sample tube. The tube was then filled with 1 ml of DMSO-d_6. The tube was gently shaken until the SPEEK dissolved into the DMSO-d_6. Samples were run using ^{1}H NMR. They were run at 300K with no spin. The samples were scanned 16 times to obtain a sharp spectrum image.

Figure 10 shows an example of a ^{1}H NMR spectrum for a sample of SPEEK with a 58.3% degree of sulphonation. It is split into three different integrations. The three integrations have the chemical shifts of:

1) I_1 – 7.60 to 7.90 ppm
2) I_2 – 7.40 to 7.55 ppm
3) I_3 – 6.85 to 7.35 ppm

The first integration (I_1) encompasses 4 protons that are common to both a PEEK monomer and a SPEEK monomer. They are labeled as 7 and 8 in Figure 10. The second integration (I_2) shows only one proton that is only found on a SPEEK monomer. It is labeled as 2' in Figure 10. The third integration (I_3) encompasses the rest of the protons, which are 8 from the PEEK monomer and 6 from the SPEEK monomer. They are labeled as 1-6, 1', and 4' in Figure 10. The proton on the SO_3H ion does not fall within the range shown in Figure 10.

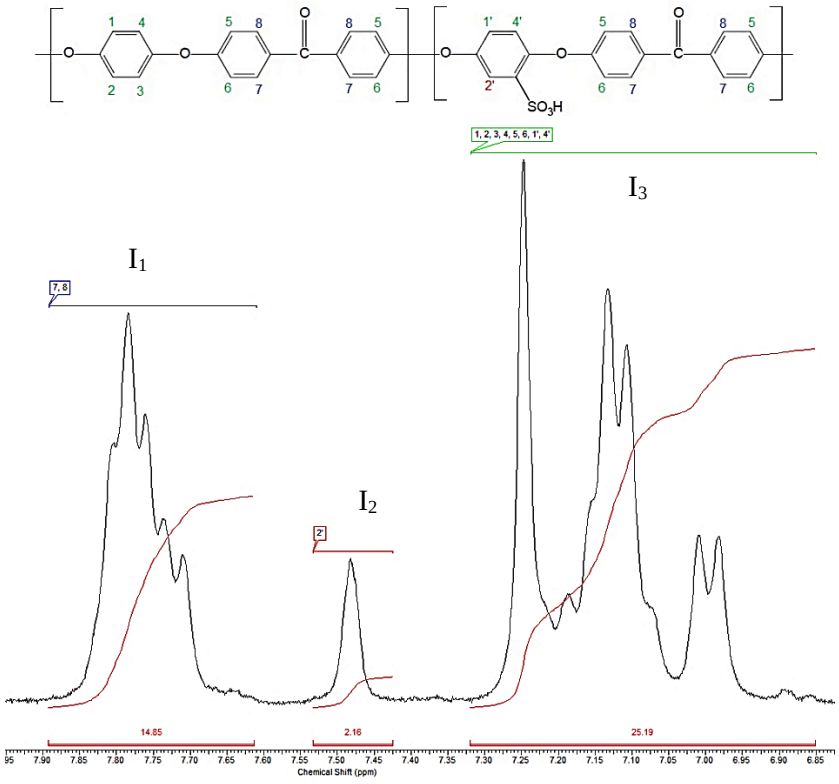

Figure 10: ^{1}H NMR Spectrum of 58.3% SPEEK with Proton Assignments

To determine the DS from these integrations, equations 18 and 19 were formulated. Equation 18 uses a ratio of I_2 to I_1 to calculate DS, whereas, equation 19 uses a ratio of I_3 to I_2. Ideally both equations provide the same result, but due to peak resolution on the NMR, these numbers can be slightly different. For this paper, all DS values determined by NMR were an average of both equations.

$$DS = \frac{I_2}{I_1/4} \tag{18}$$

$$DS = \frac{I_2}{(2I_2+I_3)/8} \tag{19}$$

The EDS was used to determine the DS for the catalyst pellets. It counts the number of Carbon, Oxygen, and Sulphur atoms near the surface of a sample and returns an atomic ratio of the three atoms that can be used to calculate the DS. A sample report can be seen in Figure 11. This sample shows an atomic ratio of 32.31% carbon, 0.77% sulfur, and 66.92% oxygen. The oxygen that is detected can be from water that has been absorbed by the catalyst, so to calculate the DS, a ratio of the carbon percentage and the sulfur percentage was used.

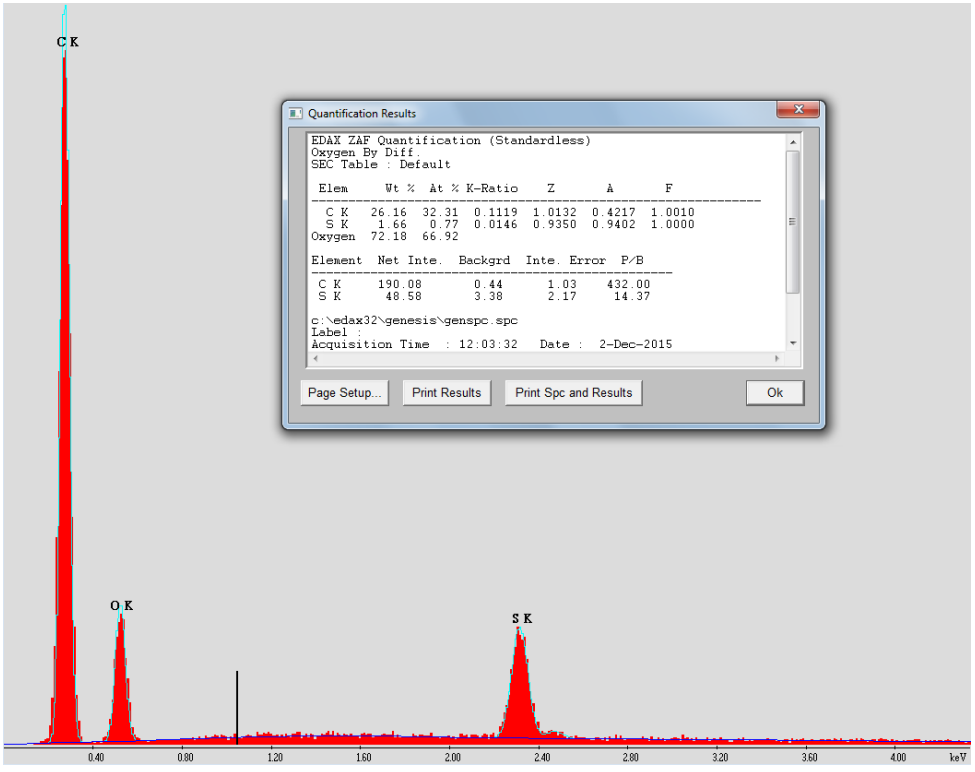

Figure 11: Sample EDX report showing a carbon peak at 0.3 keV, an oxygen peak at 0.5 keV, and a sulfur peak at 2.3 keV.

To determine the degree of sulphonation from the EDX, equation 20 was used. This equation compares the atomic percentage of sulfur that was measured (At%S) by the EDX to the atomic fraction of sulfur that is found in SPEEK. To find the atomic fraction of sulfur, the atomic count of carbon and sulfur for a sulfonated monomer is used, which are 19 and 1 respectively. The atomic fraction of sulfur in a sulfonated monomer is 1/20 or 0.05. This is used to normalize the DS so that it falls within a range of zero to one.

$$DS = \frac{\frac{At\%S}{(At\%S+At\%C)}}{0.05} \quad (20)$$

For the example spectrum in Figure 11 the DS is 0.47.

3.4 Phase 2 – Transesterification

In this phase of the experimentation, triacetin was reacted with methanol to form glycerol and methyl acetate. This is the same reaction as the biodiesel reaction. It was conducted in four different stages. The first stage used 18 molar sulphuric acid as a homogeneous catalyst, the second stage used SPEEK with a DS of 1.0 as a homogeneous catalyst, the third stage used pellets of SPEEK as a heterogeneous catalyst, and the fourth stage reused SPEEK pellets in a heterogeneous catalyst to determine their longevity. A summary of the chemical properties of each chemical can be seen in Table 10.

The experiments conducted in this phase were conducted using the same methodology. This was done to ensure that the results from one stage were directly comparable to the other stages.

Triacetin was used for these reactions to eliminate the uncertainty that is created by the phase separation that occurs when natural oils are used. Triacetin also has a standard chain length for its fatty acid, which is generally not found in most natural oils.

The reaction was run at 50°C so that the methyl acetate would not evaporate out of the solution. Keeping the methyl acetate in solution allows for a reverse reaction that would be similar to a transesterification reaction of triglycerides, where the product is not volatile.

Table 10: Chemical properties for the chemicals used in the transesterification reaction. *denotes values that are for polymer monomers.

Chemical Name	Chemical Formula	Molecular Weight (g/mol)	Melting Point (°C)	Boiling Point (°C)	Density (g/ml)
Reactants					
Triacetin	$C_9H_{14}O_6$	218.21	-78	259	1.16
Methanol	CH_3OH	32.04	-96.7	64.7	0.791
Products					
Glycerol	$C_3H_8O_3$	92.09	17.8	290	1.26
Methyl Acetate	$C_3H_6O_2$	74.08	-98	57.1	0.932
Catalysts					
Sulphuric Acid	H_2SO_4	98.078	10	337	1.84
PEEK	$C_{19}H_{12}O_3$*	288*	580	-	1.3
SPEEK	$C_{19}H_{12}O_6S$*	368*	330	-	1.3

The methanol to triacetin ratio was kept at a 6:1 molar ratio for all experiments. This is a typical ratio used for base catalyzed reactions. It was used for these experiments to minimize the materials required for each reaction as well as give results that can easily be compared to literature.

The transesterification reactions were conducted in a round bottom flask, with the same set up as the PEEK sulfonation. A diagram of the setup can be seen in Figure 9. A constant temperature bath was used throughout the experiment. A thermometer was put into the reaction to ensure that the reaction temperature was the same as the bath temperature. To prevent evaporation, a condenser was used to keep the methanol and methyl acetate in the reaction vessel. A magnetic stir rod was used in the reaction vessel to maintain constant mixing. The magnetic stir rod was maintained at an equipment setting of 1000rpm to ensure consistency between experiments. After every reaction, the vessel was removed from the constant temperature bath, cleaned and dried before being used again.

3.4.1 Transesterification using a homogenous sulphuric acid catalyst

The goal of this stage was to establish a baseline reaction rate that can be used as a comparison for the rest of this phase. Sulphuric acid is one of the most common acid catalysts used for transesterification. For this reason it was selected as the baseline. The weight of 18M sulphuric acid catalyst used was 0.5% of the weight of the triacetin used. This equates to 0.022 moles of H^+ ions per mole of triacetin.

Approximately 100g of triacetin was added to the reaction vessel. It was allowed to preheat before the methanol and catalyst were added. A measured amount of 18M sulphuric acid was dissolved in approximately 88g of methanol before it was added to the reaction vessel. After the catalyst was added to the reaction vessel the reaction timer was started.

Solution samples were taken every 20 minutes for the duration of the reaction. The experiment was conducted three times to ensure results were statistically significant and to ensure that the process was repeatable.

Approximately 5 ml were taken and mixed with 1g of calcium oxide. The calcium oxide neutralized the catalyst to stop the reaction. The mixture was shaken for 10 seconds to ensure the calcium oxide was able to neutralize all of the catalyst. After resting for 5 minutes, the sample was then centrifuged at 3300 RPM for 10 minutes to separate the solid calcium oxide from the liquid sample. For the dissolved SPEEK catalyst reactions this step was conducted three times to eliminate all of the catalyst from the sample. The sample was then placed in a clean, labeled vial to await characterization.

3.4.2 Transesterification using a homogeneous SPEEK catalyst

The goal of this stage was to determine if a homogeneous SPEEK catalyst would effectively catalyze a transesterification reaction. To ensure that the results from this stage were comparable to the H_2SO_4 baseline SPEEK with a DS of 1.0 was used with the same normality as the sulphuric acid above. For the sulphuric acid reaction, 5 g of H_2SO_4 was used per 100g of triacetin. For SPEEK with a DS of 1.0, this equates to 3.76g of SPEEK per 100g of triacetin.

Approximately 100g of triacetin and 88g of methanol were added to the reaction vessel and allowed to preheat. Once the reaction mixture was at the specified temperature, SPEEK with a DS of 1.0 was added and the reaction timer was started.

When using SPEEK as a catalyst, the normality was calculated so that it could be added in the same proportion as sulphuric acid. To calculate the weight of SPEEK required to be equivalent to the amount of sulphuric acid used, the below formula was used.

$$\text{Moles of } H^+ \text{ in } H_2SO_4 = \text{Moles of } H^+ \text{ in SPEEK}$$

Which can be broken down into:

$$\frac{(\text{H2SO4 weight}) * (\text{H2SO4 active sites})}{(\text{H2SO4 MW})} = \frac{(\text{SPEEK weight}) * (\text{SPEEK active sites})}{(\text{SPEEK MW})} \qquad (21)$$

This can be rearranged to give us the ratio of SPEEK to H_2SO_4 required for normality.

$$\frac{SPEEK\ weight}{\text{H2SO4 weight}} = \frac{(\text{SPEEK MW})*(\text{H2SO4 active sites})}{(\text{H2SO4 MW})*(\text{SPEEK active sites})} \quad (22)$$

When

$$\frac{SPEEK\ weight}{.5\ g} = \frac{\left(368\frac{g}{mol}\right)*(2)}{\left(98\frac{g}{mol}\right)*(1)} \quad (23)$$

Which means that the amount of 100% converted SPEEK required to be equivalent to 0.5g of H_2SO_4 is 3.76g.

Solution samples were taken every 20 minutes for the duration of the reaction. The experiment was conducted three times to ensure results were statistically significant and to ensure that the process was repeatable. Samples were treated in the same manner as the samples taken for the sulphuric acid catalyst.

3.4.3 Transesterification using a heterogeneous SPEEK catalyst

The goal of this stage was to determine if a heterogeneous SPEEK catalyst can catalyze a transesterification reaction. Due to the uncertainty of the surface area of the catalyst, the concentration of H^+ ions were not calculated.

The catalyst was dried and then weighed. It was then submerged in 25°C methanol for 24 hours and weighed again. This was done to allow the pellets to absorb methanol before they were introduced into the reaction medium. This step was done to ensure that the pellets were able to start catalyzing the reaction as soon as they were introduced and did not cause a lag while they absorbed methanol from the reaction solution.

Approximately 100g of triacetin and 88g of methanol, minus the methanol that was absorbed by the catalyst, were added to the reaction vessel and allowed to preheat. Once the reaction mixture was at the specified temperature, the SPEEK pellets were added and the reaction timer was started.

Solution samples were taken every hour for the duration of the reaction over a period of 24 hours. The experiment was conducted two times for two different batches of SPEEK pellets. Samples were treated in the same manner as the samples taken for the sulphuric acid catalyst.

3.4.4 Durability of the heterogeneous SPEEK catalyst

The procedure for this phase was the same as the previous phase. The two batches of SPEEK pellets were combined to increase the catalyst density in the reaction mixture for these experiments. The experiment with the combined batches was conducted seven times to evaluate if there was a drop in the reaction rate after repeated uses.

3.4.5 Sample characterization

To determine transesterification conversion as a function of reaction time NMR spectroscopy was used. Each sample contained the following chemicals, their chemical structures can be seen in Figure 12:

- Methanol
- Triacetin
- Diacetin
- Monoacetin
- Glycerol
- Methyl Acetate

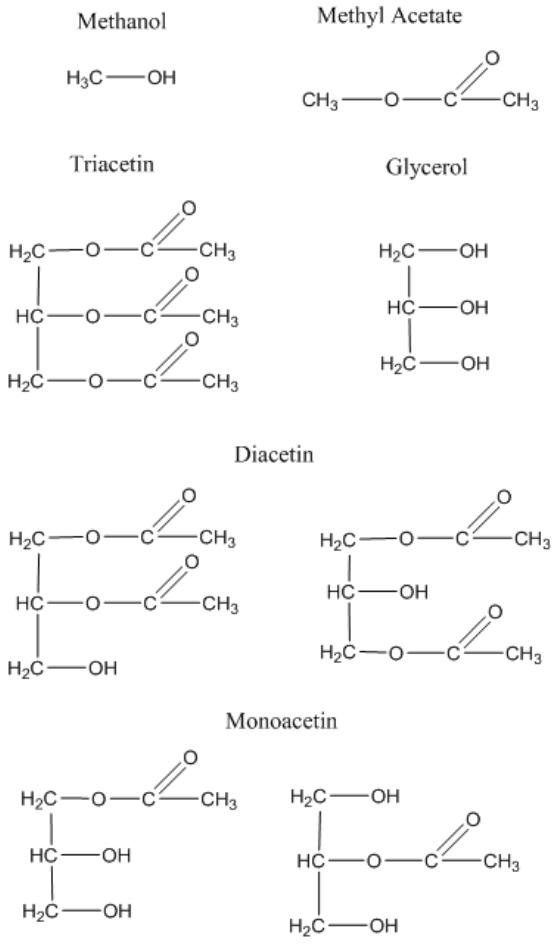

Figure 12: Chemical structures for each of the chemicals found in the transesterification reaction and their isomers.

Table 11 shows all of the NMR peaks and their chemical shifts that can be found in a solution sample. A representative NMR spectrum of one of the samples can be seen in Figure 13. This was a sample taken from a reaction where 26% of the triacetin chains were converted into methyl acetate. As can be seen in the figure, there are a number of overlapping peaks in the range of 3.8 to 4.4 ppm. There are also a number of overlapping peaks from hydrogen configurations that are common to more than one molecule, such as the $–CH_3$ that has a chemical shift of 1.8-2.2 and can be found in triacetin, diacetin, monoacetin, and methyl acetate. Because of these overlapping peaks, it is impossible to determine the ratios of the 6 different chemical species that are in the sample based on all available peaks. Spectrum analysis focused on those peaks that could reveal the conversion achieved during transesterification.

Table 11: NMR peak location based on chemical shifts for each of the chemicals found in a sample transesterification.[86]

Chemical	Hydrogen Placement	Chemical Shift (PPM)
Methanol	$-CH_3$	3.1-3.2
	-OH	4.0-4.6
Triacetin	$-CH_2-$	4.0-4.3
	-CH-	5.0-5.3
	$-CH_3$	1.8-2.2
Diacetin	$-CH_2-$	3.2-4.3
	-CH-	4.4-5.0
	$-CH_3$	1.8-2.2
	-OH	4.0-4.6
Monoacetin	$-CH_2-$	3.2-4.3
	-CH-	4.4-5.0
	$-CH_3$	1.8-2.2
	-OH	4.0-4.6
Glycerol	$-CH_2-$	3.2-3.7
	-CH-	3.2-3.7
	-OH	4.0-4.6
Methyl Acetate	$-OCH_3$	3.5-3.6
	$-CH_3$	1.8-2.2

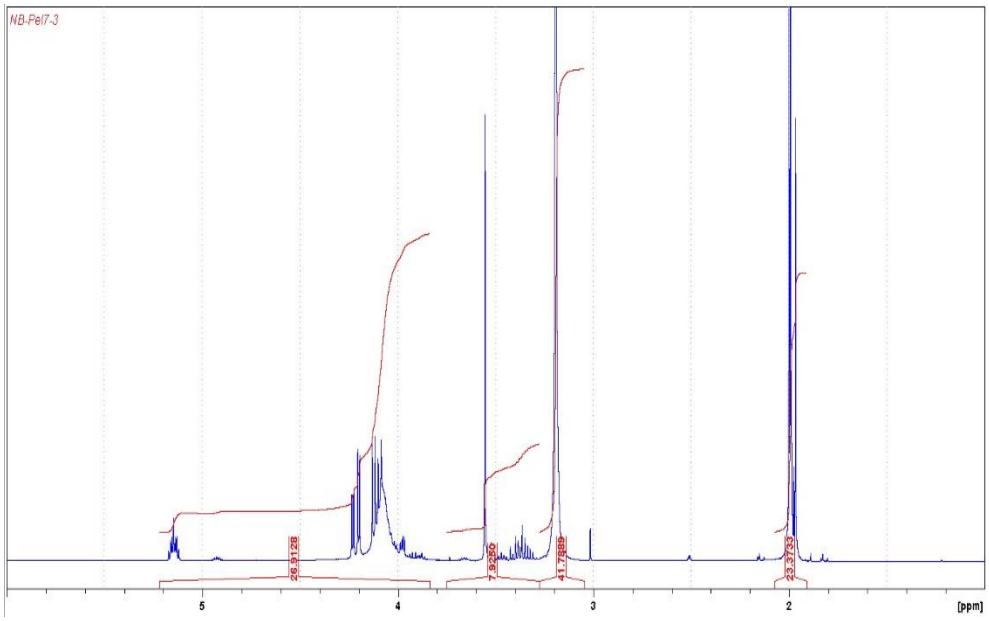

Figure 13: An example NMR with the 4 integration zones highlighted

There were two methods to determine conversion. The ratio of the methyl acetate peak at 3.6 could be compared to the methyl group peak at 2.0 which contains all reacted and unreacted ester chains. This will give a conversion based off of the amount of methyl acetate in the reaction solution. This method was not chosen because the reaction was conducted close to the boiling point of methyl acetate, and the amount of methyl acetate lost to vaporization is unknown. This method would give a conversion that is lower than is expected. The method chosen, which is described in the next few pages, uses the hydrogen on the backbone of the triacetin and glycerol to determine conversion. The method used gives a conversion that is slightly higher than is expected at lower conversions due to the uncertainty of the alcohol peak. It was chosen because it is more accurate across the whole reaction.

To simplify the list of molecules to distinguish between, triacetin, diacetin, monoacetin and glycerol were broken down into the sub-molecules seen in Figure 14. This reduced the number of species to distinguish between to 4. They are:

- Methanol
- Reacted Chain
- Unreacted Chain
- Methyl Acetate

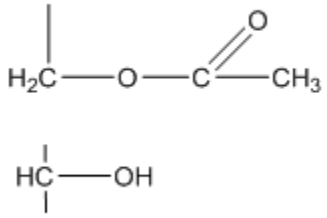

Figure 14: Unreacted (top) and reacted (bottom) chains of a triacetin molecule

For the reacted FA chain and unreacted FA chain on the triacetin, each group generate three peaks on an NMR spectrum. These can be seen in Table 12.

Table 12: Chemical shifts for the simplified sub-molecules "Reacted Chain" and "Unreacted Chain"

Chemical	Hydrogen Placement	Chemical Shift (PPM)
Unreacted Chain	$-CH_2-$	4.0-4.3
	-CH-	5.0-5.3
	$-CH_3$	1.8-2.2
Reacted Chain	$-CH_2-$	3.2-4.3
	-CH-	3.2-4.3
	-OH	4.0-4.6

To determine the ratio of the four different chemicals the peaks on the NMR spectrum were grouped into four different regions. These regions can be seen in Figure 13. Each region can be quantified by its integration. Table 13 outlines the four integration zones, and the chemical shifts associated with each of them. It also shows the number of protons in each integration, broken down by which chemical they belong to. From this table, we can determine what is in each integration region and derive a formula to calculate it using the concentration of the chemicals in solution as variables. These can be seen in equations 24-27. From these four equations, the concentration of each chemical can be determined. They can be seen in equations 28-31.

Table 13: Integration ranges for each individual chemical in the reaction mixture with number of hydrogen in each integration

	Chemical Shift Ranges			
Chemical	I_1 (5.5-4.5)	I_2 (4.5-3.8)	I_3 (3.7-3.2)	I_4 (2.5-1.0)
Unreacted Chain (A)	1_a (5/3)			4_a (3)
Reacted Chain (D)	1_d (1)	2_d (5/3)		
Methanol (Me)	1_{Me} (1)		3_{Me} (3)	
Methyl Acetate (Ma)		2_{Ma} (3)		4_{Ma} (3)

To separate the number of protons on the glycerol backbone of the triacetin into the groups from above, the total number of protons from the backbone, 5, was divided by the number of sub-molecules that it was separated into, 3, to give a fractional molecule of 5/3 that occupied that site. For the purposes of calculating the yield from NMR integrations each of the three carbons on the glycerol backbone was assumed to have 5/3 protons. Because the integration ranges combined the peaks of all 5 protons into one integration, this was considered a valid assumption.

$$I_1 = 1_a A + 1_d D + 1_{Me} Me \tag{24}$$

$$I_2 = 2_d D + 2_{Ma} Ma \tag{25}$$

$$I_3 = 3_{Me} Me \tag{26}$$

$$I_4 = 4_a A + 4_{Ma} Ma \tag{27}$$

$$Methanol = \frac{I_3}{3_{Me}} = \frac{I_3}{3} \tag{28}$$

$$Methyl\ Acetate = \frac{I_4}{4_{Ma}} - \frac{4_a(A)}{4_{Ma}} = \frac{I_4}{3} - A \tag{29}$$

$$Reacted\ Chain(D) = \frac{I_2}{2_d} - \frac{2_{Ma} I_4}{4_{Ma} 2_d} + \frac{2_{Ma} 4_a(A)}{2_d\ 4_{Ma}} = \frac{3}{5}(I_2 - I_4 + 3A) \qquad (30)$$

$$Unreacted\ Chain(A) =$$

$$\frac{I_1 - \frac{1_d I_2}{2_d} + \frac{1_d\ 2_{Ma} I_4}{4_{Ma}\ 2_d} - \frac{1_{Me} I_3}{3_{Me}}}{1_a + \frac{1_d\ 2_{Ma}\ 4_a}{2_d 4_{Ma}}} = \frac{15}{52}\left(I_1 - \frac{3}{5} I_2 - \frac{1}{3} I_3 + \frac{3}{5} I_4\right) \qquad (31)$$

The glycerol backbone of the Tri, Di and Monoacetin was a complicating factor in this method. The protons on the backbone appear anywhere from 5.5 to 3.8 PPM on the NMR spectrum. The location of their peak changed depending on which of the three chains had reacted.

In this chapter the resources used to conduct the two proposed phases of research, and the experimental conditions of those two phases are outlined. In the next chapter the results for these experiments are examined.

4 Results and Discussion

This chapter is broken down into the two different phases, PEEK sulphonation and transesterification.

In phase one, the solubility rates are examined to determine the best concentration of sulphuric acid to use when producing SPEEK. A mathematical model for the rate of sulphonation was applied against the experimental results obtained from NMR spectroscopy. Finally, SPEEK catalyst pellets were produced using the information obtained from the solubility and sulphonation of PEEK in sulphuric acid parts of this phase and characterized using SEM and EDX.

In phase two, a baseline was set for the transesterification of triacetin in methanol using homogeneous sulphuric acid as the catalyst. SPEEK with a DS of 1.0 was then used as a homogeneous catalyst and compared to the sulphuric acid baseline. The SPEEK catalyst pellets that were produced in phase one were then used for transesterification. All transesterification conversion results were obtained using NMR spectroscopy and presented along existing kinetic models. Finally, the SPEEK catalyst pellets were examined for their durability using SEM and their effectiveness as catalysts following multiple transesterification reactions.

4.1 Phase 1 - PEEK Sulphonation

4.1.1 Solubility rates

The solubility of PEEK in sulphuric acid depends on three factors: the temperature, the concentration of the sulphuric acid, and the degree of sulphonation. When the solution is mixed, the rate of solvation increases and PEEK is distributed evenly throughout the sulphuric acid. Without mixing PEEK will dissolve and float on top of the sulphuric acid. When PEEK dissolves into sulphuric acid, the acid turns a yellow colour, as can be seen in Figure 15. As the concentration of PEEK dissolved in the sulphuric acid increases, it turns a dark orange colour. This can be used as a visual indicator for how much PEEK has been dissolved in the sulphuric acid.

Figure 15 shows the solvation of PEEK tubing in varying concentrations of sulphuric acid at 25°C. The acid concentrations are (from left to right) 94%, 92.5%, 90%, 87.5%, and 85%. The top set of test tubes are a photo after 5 hours of submersion, and the bottom set of test tubes are a photo after 25 hours of submersion.

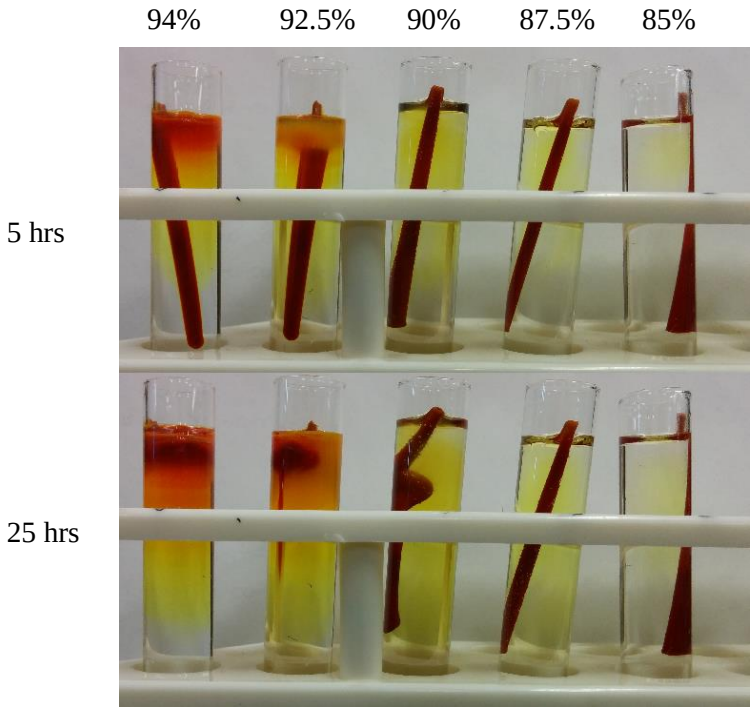

Figure 15: PEEK dissolving in Sulphuric acid at 5 hours and 25 hours (top and bottom respectively) at a temperature of 25°C. The acid concentrations are (from left to right) 94%, 92.5%, 90%, 87.5%, and 85%.

It can be seen that in the 94% sulphuric acid, the PEEK tubing loses structural integrity and forms a clump at the surface of the sulphuric acid. After 25 hours, the PEEK tube in the 90% sulphuric acid is also losing its structural integrity. The PEEK tube in the 85% sulphuric acid shows very little signs of dissolving although there is a slight discolouration of the sulphuric acid around the tube. Because the density of the PEEK tubing is less than that of the sulphuric acid, it floats on the top of the acid.

An acid gradient forms between the sample and the bulk acid because the samples were not stirred. This occurs due to water being generated during the sulphonation reaction. This had the effect of reducing the reaction rate at the surface. As the concentration of sulphuric acid decreases, the reaction rate also decreases. This has an effect on the rate in which the PEEK will dissolve.

The rate of solvation of PEEK in sulphuric acid had a large role in the production of the catalyst. In order to produce a catalyst that has a core of PEEK, and has an outer shell of SPEEK, a balance had to be found between the reaction rate and the solvation rate of the PEEK.

4.1.2 Kinetic rates

Phase one was designed to test the accuracy of a mathematical model that predicts the kinetic rate of the sulphonation of PEEK. The model equation for the reaction is shown in equation 32. This equation is derived from equations 8, 10, 14 and 15. It contains the reaction variables of temperature, sulphuric acid and water concentrations, time, and conversion.

$$\frac{[H_2SO_4]^x}{[H_2O]^y} = C_s \tag{8}$$

$$kC_s = k_1 \tag{10}$$

$$-Ln(1-X) = k_1 t \tag{14}$$

$$k = k_o\, e^{\frac{-Ea}{RT}} \tag{15}$$

$$-\ln(1-X) = \frac{[H_2SO_4]^x}{[H_2O]^y}\; k_o\, t\, e^{-\frac{E_a}{RT}} \tag{32}$$

Due to the solubility limits of PEEK into sulphuric acid, the concentrations of sulphuric acid and water have an insignificant change for the duration of a sulphonation reaction. Because of this small change, it is assumed that the concentrations are constant, which is represented by equation 8. The constant value is then rolled into the kinetic constant in equation 14. This creates a problem when calculating the activation energy for the reaction. Researchers who use different starting concentrations of sulphuric acid have obtained different Ea values. This can be seen in Table 14.

Putting these equations together is a novel idea. When PEEK is dissolved in a sulphuric acid solution that is constantly stirred, the amount of sulphuric acid used in the reaction is so small it does not affect the concentration of sulphuric acid in the bulk solution. This made it very easy to assume that the concentration ratio was constant, which is represented by equation 8. This was the focus for all of the previous research that was conducted.

For unstirred reactions, concentration gradients form between the reacting PEEK and the bulk acid solution. In this situation, the concentration of sulphuric acid varies with location. Equation 31 allows for a more in depth model that can take these gradients into account. As future work, a computer model can be created that can track the acid concentration and predict the DS for different areas around a SPEEK catalyst pellet.

Table 14: Constant values, from three various sources, for the equation that models the reaction speed of the sulphonation of PEEK.

Constant	Values [81]	Values [78]	Values [22]
x	2		
y	2.3		
k_o		$1.31x10^{11}$ L/molh	
E_a		18.8 kcal/mol	20.4kcal/mol
Temp Range		22-55°C	25-75°C

Due to the variations in E_a values, the experiments outlined in Table 15 were conducted to determine the kinetic constants of k_0 and E_a for this research. The reactions were conducted at three different temperatures, 70°C, 60°C and 40°C. The results from these reactions are shown in Figure 16.

In Figure 16, –ln(1-X) is reported as a function of reaction time, where the slope of the line is equal to the kinetic constant, k_1, in accordance with equation 14. k_1 is a temperature dependent constant. At 70°C it is 0.66±0.07 hr^{-1}, at 60°C it is 0.33±0.01 hr^{-1} and at 40°C it is 0.049±0.003 hr^{-1}. The error analysis can be found in Appendix B. Equation 10 shows the relationship between k and k_1. Using the x and y constants shown in Table 14, 94% sulphuric acid has a Cs of 4.81. The sulphuric acid used in the lab was titrated and found to have a concentration of 94% acid. The kinetic constants at the three temperatures mentioned above allow the use of Arrhenius equation, equation 16, to determine what E_a and k_0 for the conditions used in this research.

Table 15: PEEK concentrations in a sulphuric acid solution to determine the kinetics for the sulphonation of PEEK.

Trial Name	Temperature (°C)	M_{PEEK} (g)	M_{H2SO4} (g)	[PEEK] (g/cm^3)
SPEEK1	70	6.30	246.36	0.045
SPEEK2	60	6.34	255.80	0.044
SPEEK3	40	6.32	224.02	0.050
SPEEK4	60	6.40	222.53	0.051

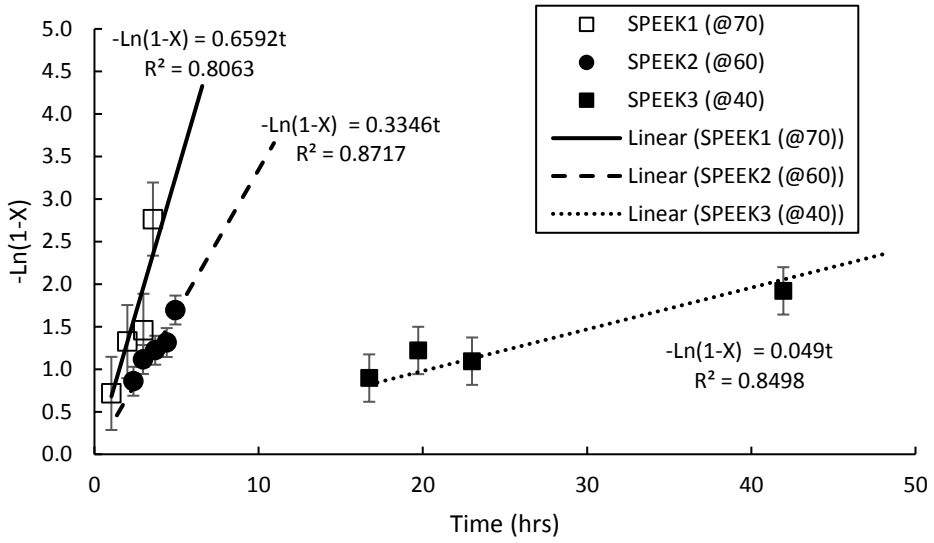

Figure 16: Determination of constant k_1 for the sulphonation of PEEK at three different temperatures.

Figure 17 shows the plot of LnK versus the temperature reciprocal for the experimental data. From equation 16, the slope of the line is equal to $-E_a/R$ and the intercept of the line is equal to LnK_0. With a slope of -9430±540 K and an intercept of 25.5±1.6, the calculated E_a and K_0 are 78.5±4.6 kJ/mol and $1.24\pm0.08\times10^{11}$ L/mol h respectively. Due to the error that is carried through from figure 16, the error for the Ea value is 6%. Details on how the error was calculated can be found in Appendix B. The calculated value closely match that found by Huang et al. [78]. These values are used in the model.

Figure 19 and 20 show the degree of sulphonation of PEEK in concentrated sulphuric acid as a function of reaction time. The kinetic model of equation 31, with the constant determined above, is also compared to the experimental data in both Figure 18 and Figure 19. In Figure 18 the data from two separate experiments that were run at 60°C both follow the model curve closely. The data from the trial "SPEEK 1" which was conducted at 70°C also follows the model curve closely. In Figure 19 the data from the trial "SPEEK 3" closely follow the model data for a reaction at 40°C. From these experiments, it can be seen that the model works well for determining the conversion of PEEK to SPEEK. This data was used when developing the method to produce a solid acid catalyst pellets.

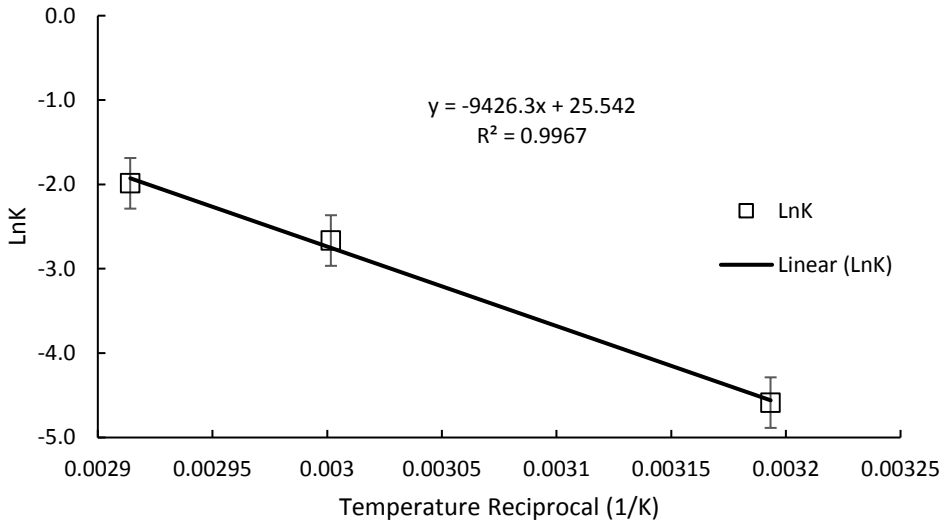

Figure 17: Plot of LnK vs the temperature reciprocal for the sulphonation of PEEK

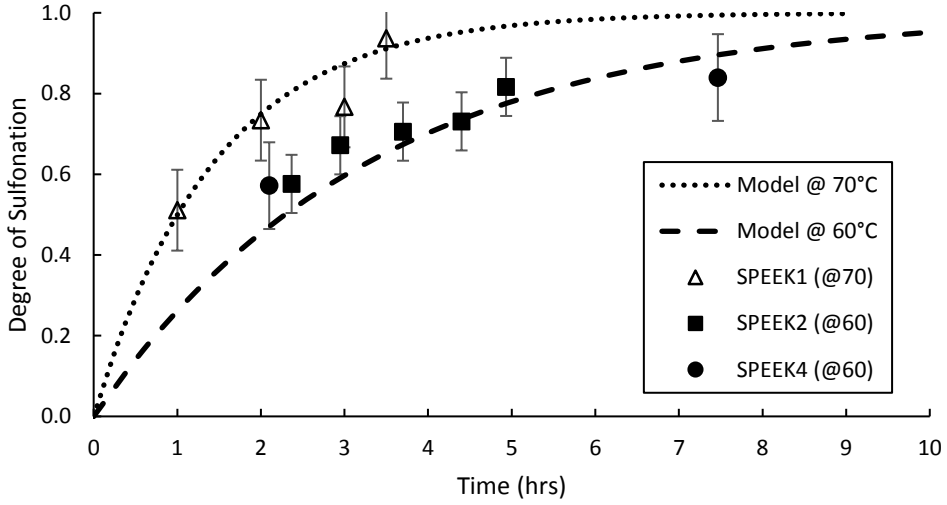

Figure 18: Model for sulphonation of PEEK compared to experimental data. SPEEK 1 was run at 70°C and SPEEK 2 and 4 were run at 60°C.

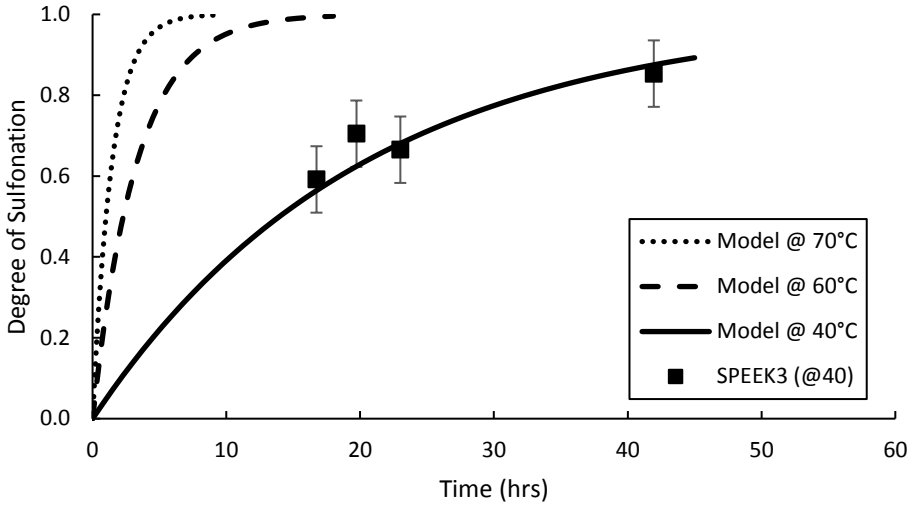

Figure 19: Model for sulphonation of PEEK compared to experimental data. SPEEK 3 was run at 40°C.

The sulphonation reactions were allowed to run to completion for the production of a homogeneous SPEEK catalyst with a DS of 1.0. After the first wash the catalyst was an opaque white colour. When the SPEEK was dried, the SPEEK shrank and changed colour to a clear dark yellow. An oven was used at a temperature of 80°C for a period of 24 hours to remove the water from the samples. If left in the open air, the samples would absorb water from the humidity in the air.

The kinetic rate of sulphonation of PEEK had a large role in the creation of the catalyst. In order to produce a catalyst that has a core of PEEK, and has an outer shell of SPEEK, a balance must be found between the reaction rate and solvation rate of PEEK.

4.1.3 Catalyst pellets

Catalyst pellets consisting of a shell of SPEEK on a core of PEEK were produced as described in section 3.3.3 in 94% sulphuric acid.

After the reaction the SPEEK disc was a dark orange colour. The disc consisted of a solid core with partially dissolved SPEEK forming a gel around it. Taking the catalyst out of the test tube deformed the shape of the pellets so that they were no longer a geometric shape. When placed in a water bath, the surrounding gel solidified. During this water bath, the pellets absorbed water and changed colour to white. Areas that were not sulfonated stayed a yellow/orange colour. The end product was a white pellet that had the occasional bit of yellow showing. An example of this can be seen in the right hand side of Figure 20.

During the first two water washes, visible particles of SPEEK detached from the catalyst pellets. During the third water wash, the water came out clear. During the boiling methanol wash, the pellets again lost small particles from their surface. After the third boiling methanol wash, the methanol was clear. A pH strip was used to verify that the methanol exiting the wash was neutral. When the pellets were dehydrated, they turned an opaque yellow/orange colour.

The surface of each pellet ranged from smooth to rough, depending on factors such as the amount of sulphuric acid trapped in the gel phase and the mechanical handling of the catalyst pellet before it was submerged in the water wash.

Figure 20: SPEEK pellets used as the catalyst. The left shows what they look like when dehydrated, and the right shows how they look when they absorb methanol.

Figure 21 shows a SEM photo of one of the catalyst pellets. The rough surface shown was created during the removal of sulphuric acid that was trapped in the gel phase of the catalyst pellet. When the pellet is submerged in water, the partially dissolved SPEEK surrounding the PEEK core solidifies. This solidification traps small pockets of sulphuric acid in the catalyst. During the washing process, the trapped sulphuric acid is slowly replaced by the wash solution. As layers of SPEEK are dissolved by the washing solution, these pockets are exposed and form the texture that can be seen.

Figure 20 shows the catalyst pellets in their dehydrated state and after absorbing methanol. In the top right hand corner of the right hand photo the solid PEEK core can be seen. It is made up of a few pellets that have been linked together by the partially dissolved SPEEK.

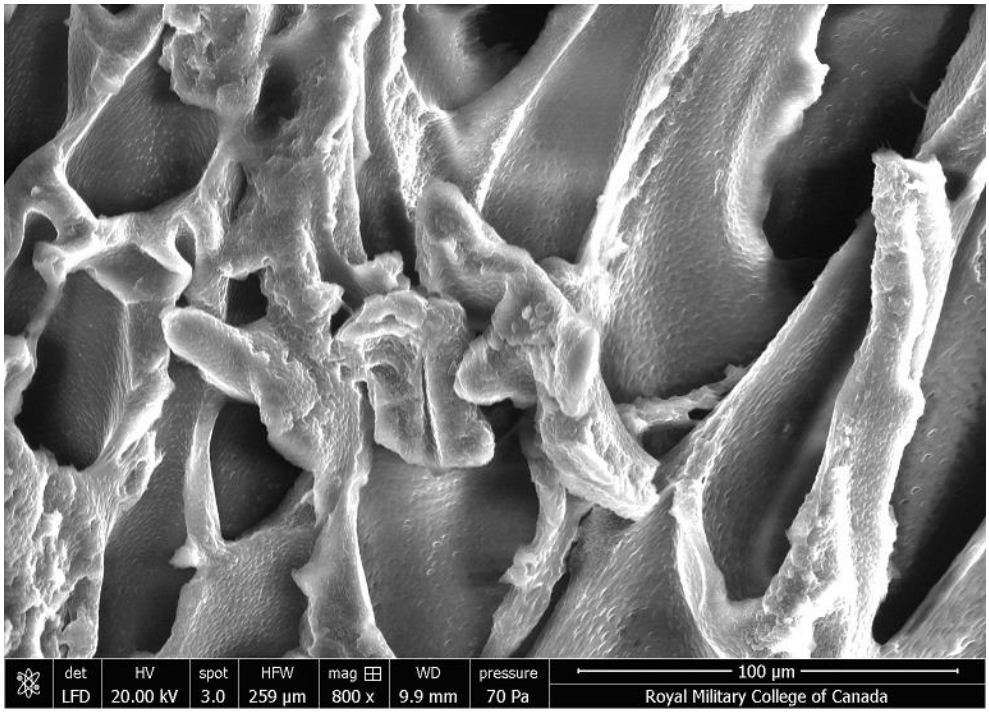

Figure 21: An electron scanning micrograph of the surface of one of the pellets of SPEEK catalyst.

An attempt was made to determine the degree of sulphonation on the surface of the catalyst pellets using NMR and EDS techniques, but both provided limited information on the DS achieved. The best deuterated solvent for dissolving SPEEK is DMSO-d6. It will dissolve SPEEK with a DS of 0.4 or greater. When SPEEK was shaved off of the surface of a catalyst pellet, the SPEEK would not dissolve in DMSO. Thus, the DS of the surface of the pellet was below 0.4. The EDS penetrated the catalyst pellets beyond the surface, which allowed the PEEK core to skew the results lower than reality. The EDS gave results ranging from a DS of 0.12 to 0.36. Shavings from the surface of the catalyst pellets were too thin and the EDS picked up the aluminum base the shavings were sitting on. The ratio of Sulphur to Carbon in a monomer of SPEEK is low, so a sample with a low DS compounded this ratio. Because of this, the Sulphur in the SPEEK catalyst pellet samples were just above the detectability limit of the EDS.

The catalyst pellets had a poor surface area to volume ratio, but had enough surface area to determine whether or not the catalyst was effective. Future works can focus on characterizing the effectiveness of a known surface area for a given DS and creating a catalyst that has a greater surface area to volume ratio.

4.2 Phase 2 - Transesterification

4.2.1 Baseline kinetics with a homogeneous sulphuric acid catalyst

An 18 molar sulphuric acid catalyst was used to develop a benchmark that was used to compare the effectiveness of a SPEEK catalyst. The transesterification reaction using 18M sulphuric acid as a catalyst was conducted three times. This was to ensure repeatability in the process. The reactions were carried out at 50°C and had a molar ratio of triacetin:methanol of 1:6. 0.5g of sulphuric acid was used for every 100g of triacetin. Reactions were run up to 200 min in duration. The exact details of each trial can be seen in Appendix A: Table 16.

The kinetics for this reaction can be described by a second order reaction equation, which can be seen in equation 33 [87]. This is the integrated equation for two different reactants both of which are first order and start at concentrations that are not stoichiometric.

$$\frac{1}{a[B]_o - b[A]_o} \ln\left(\frac{[B]_t[A]_o}{[A]_t[B]_o}\right) = k_f t \tag{33}$$

Where: a = stoichiometric coefficient for triacetin, b = stoichiometric coefficient for methanol, $[A]_o$ = starting concentration of triacetin, $[B]_o$ = starting concentration of methanol, $[A]_t$ = current concentration of triacetin, $[B]_t$ = current concentration of methanol, k_f = kinetic constant, and t = time.

Equation 33 was used because the kinetics for transesterification have been proven to be second order. It is first order with respect to the concentration of methanol and the concentration of triglycerides. For reactions with an excess of methanol, the reaction kinetics can be simplified to pseudo first order kinetics. For the case of this experiment, using a 6:1 methanol to triglyceride ratio, the methanol concentration is not high enough to warrant the use of pseudo first order kinetics. The reaction is also reversible, although the forward reaction is favoured due to the excess of methanol, stearic hindrance, and gibbs energy. Because of this, the reverse reaction is assumed to be negligible for the conversion range studied.

For the reaction conditions of this experiment, a molar ratio of 6:1, equations 34 and 35 hold true. Where X is equal to the conversion of triglycerides into FAME. Since all of the transesterification reactions start with the same concentrations, the starting concentrations of the reactants can be assumed as constant. They are combined into the kinetic constant in Equation 36.

$$\frac{[A]_t}{[A]_o} = 1 - X \tag{34}$$

$$\frac{[B]_t}{[B]_o} = 1 - \frac{X}{2} \tag{35}$$

$$k = k_f(a[B]_o - b[A]_o) \tag{36}$$

When these equations were combined together, a linear equation, equation 37, is formed. This equation can be used to find the value of K. This value was different for each catalyst and was used as a comparison of the effectiveness of each catalyst.

$$-\ln\left(\frac{1-X}{1-\frac{x}{2}}\right) = kt \tag{37}$$

Figure 22 is a plot of the left hand side of equation 37 as a function of time. The kinetic constant that is found by the linear regression is 8.1×10^{-3} min^{-1}.

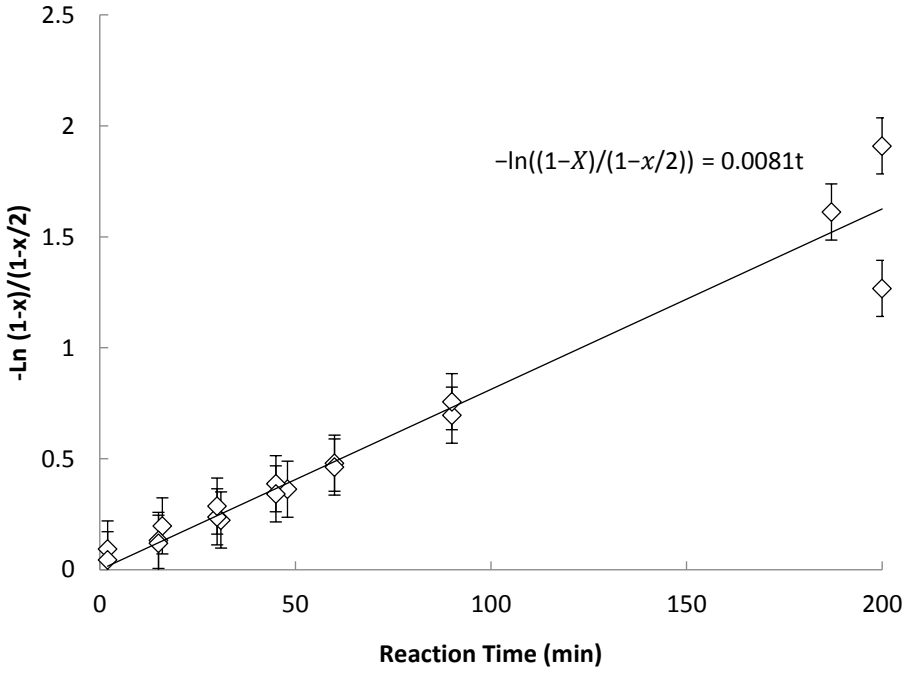

Figure 22: Trial 1 - Sulfuric acid catalyzed transesterification of triacetin at 50°C with a 6:1 methanol:triacetin ratio and 0.5g catalyst per 100g of triacetin linearization to determine the kinetic constant for the reaction.

All three of the trials matched the second order kinetics curve, which can be seen in Figure 23. In this figure, the reaction proceeds over the span of 200 minutes. They achieve a conversion of 92% in that timeframe. A detailed look at the sources of error for the transesterification process can be found in Appendix B.

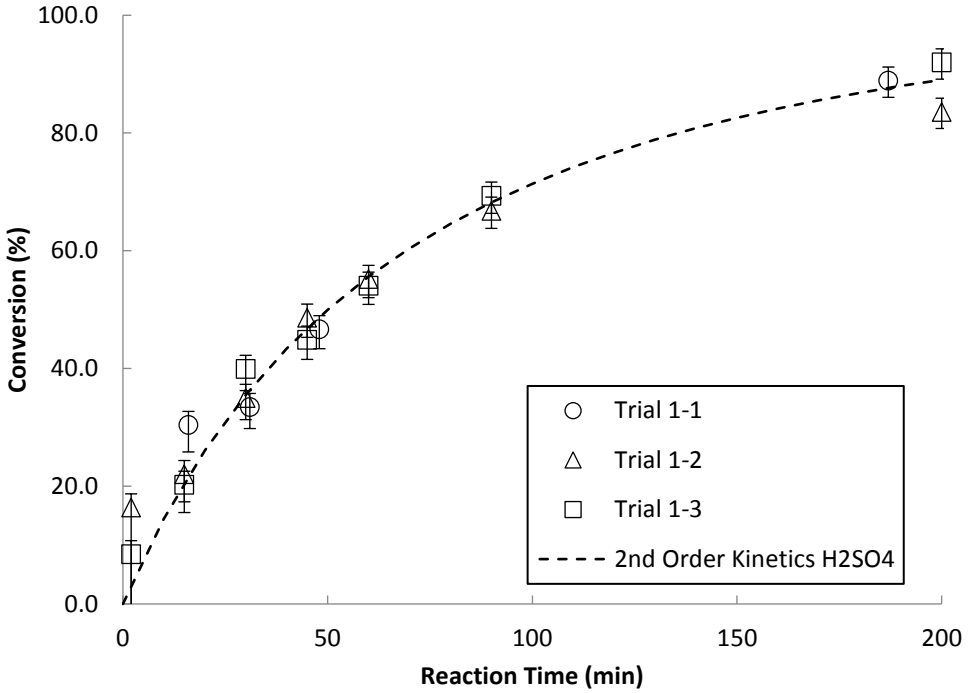

Figure 23: Trial 1 - Sulfuric acid catalyzed transesterification of triacetin at 50°C with a 6:1 methanol:triacetin ratio and 0.5g catalyst per 100g of triacetin

4.2.2 Effectiveness of SPEEK as a homogeneous catalyst

Three trials were run with a catalyst of SPEEK with a DS of 1.0. This was to ensure repeatability in the process. The reactions were carried out at 50°C and had a molar ratio of triacetin:methanol of 1:6. 3.76g of SPEEK with a DS of 1.0 was used for every 100g of triacetin. Reactions were run up to 180 min in duration. The details of each trial can be seen in Appendix A, Table 20.

These three trials matched the second order kinetics curve, which can be seen in Figure 24. The amount of catalyst used was calculated to have the same normality as the sulphuric acid catalyst. The dissociation constants were looked at for both sulphuric acid and SPEEK. There is no dissociation constant published for SPEEK, so the one for Benzenesulfonic acid was used as an approximation. At the

concentrations used for these experiments, the dissociation of SPEEK with the same normality was 27% compared to sulphuric acid.

The reactions were carried out up to a maximum of 180 min. In that time the highest conversion achieved was 78%. The kinetic constant calculated using equation 37 was found to be $7.8x10^{-3}$ min^{-1}. When compared to the baseline reaction using sulphuric acid as the catalyst, the two kinetic constants are statistically the same. A plot of the kinetic curves along with the sample data can be seen in Figure 24. The SPEEK reaction was slightly slower than that of the sulphuric acid. This slight difference can be explained by the variability in the results found using a homogeneous SPEEK catalyst.

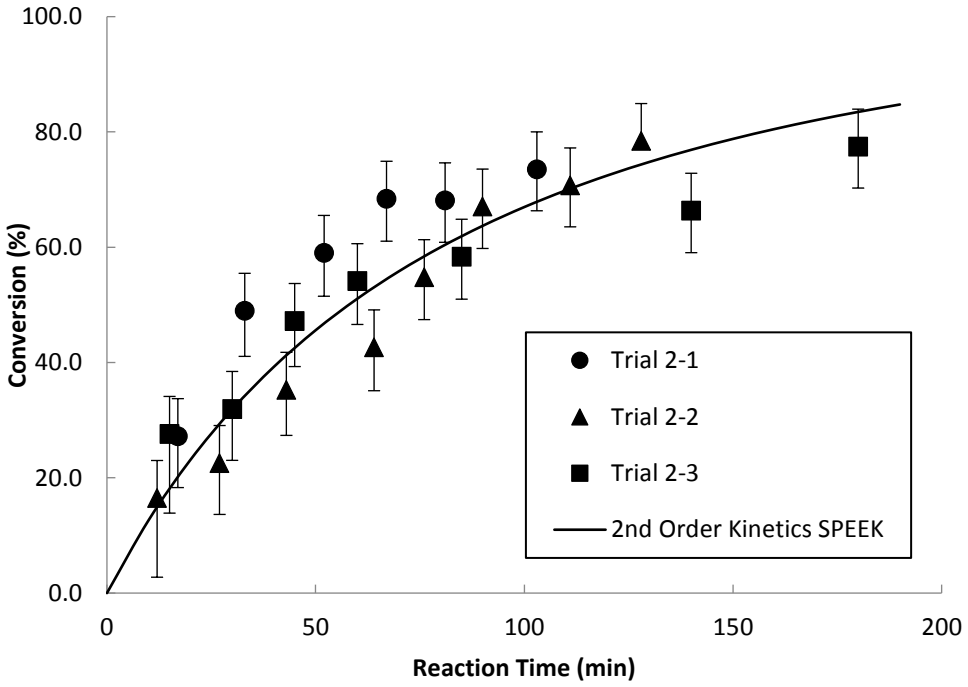

Figure 24: Trial 2 – DS 1.0 SPEEK catalyzed transesterification of triacetin at 50ºC with a 6:1 methanol:triacetin ratio and 3.76g catalyst per 100g of triacetin

The significance of these two kinetic constants matching so closely is that the SPEEK monomer has the same reactivity as sulphuric acid. The size of the SPEEK molecule does not hinder its ability to be used as a homogeneous catalyst. This finding demonstrates that SPEEK can be used as a catalyst and is just as effective as sulphuric acid. When the dissociation of the acid groupings are taken into account, the effectiveness of SPEEK as a catalyst in transesterification reactions is better than the sulphuric acid. This increased effectiveness is attributed to the

hydrophobic regions of the SPEEK backbone being more compatible with the mostly hydrophobic nature of the triglyceride.

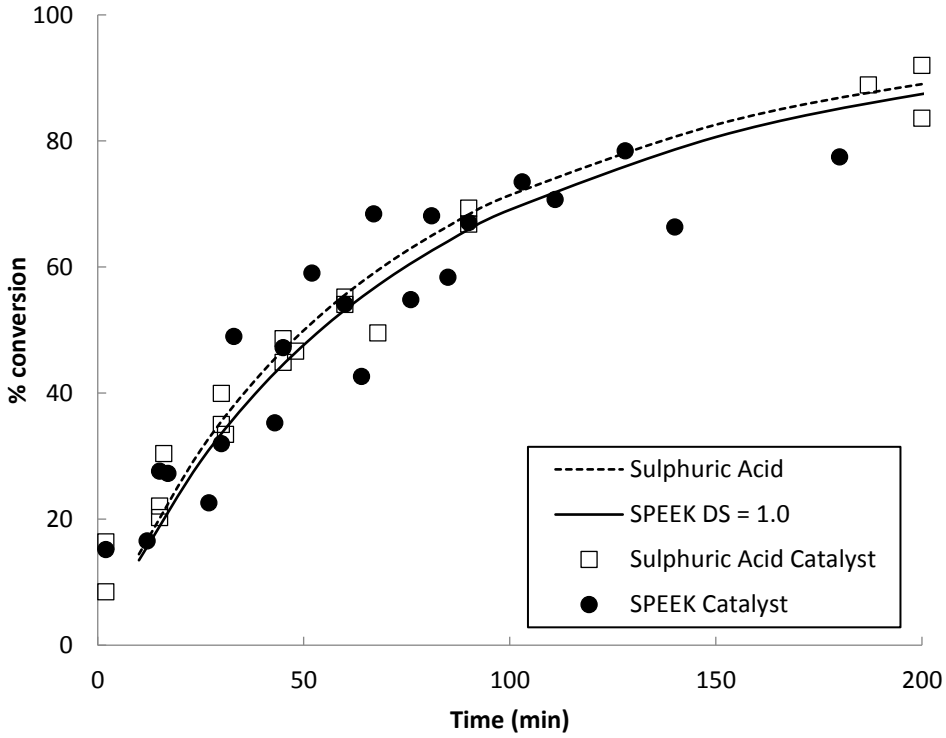

Figure 25: Comparison of Homogeneous H_2SO_4 Catalyst vs SPEEK Catalyst with a DS of 1 using second order kinetics. Error bars have been omitted for clarity.

4.2.3 Effectiveness SPEEK as a heterogeneous catalyst

Using SPEEK as a homogeneous catalyst does not make any improvement to the current transesterification practices. In order to maximize its usefulness, it must be used as a heterogeneous catalyst. Two batches of catalyst pellets were produced and were used in trials 3 and 4. The first batch had a dry weight of 21.05 g and the second batch had a dry weight of 20.67 g. All of these trials were carried out at 50°C and had a molar ratio of triacetin:methanol of 1:6. Reactions were run up to 1800 min in duration. The details of each trial can be seen in Appendix A, Table 24. The heterogeneous catalyst that was used had less active sites than the homogeneous catalysts that were examined above.

The catalyst pellets were cylinders approximately 10mm in diameter and ranging from 5mm deep to 10mm deep. They had a soft SPEEK shell around a hard PEEK

core. The process to create them is explained in section 3.3.3. Figure 20 is a picture of the catalyst used for trial 4.

Figure 26 shows the results from trial 3-1 and compares it to the results found for the homogeneous catalysts. In this trial the transesterification reaction was conducted over 1587 minutes and reached a final conversion of 90.2%. The kinetic constant for this reaction was found to be $0.9x10^{-3}$ min^{-1}. When compared to the results found using sulphuric acid, the SPEEK pellets had a kinetic constant that was 9 times smaller. The reason for the major difference in reaction rates is the availability of reaction sites on the catalyst. The pellets that were produced were not optimized for their surface area and the bulk of the catalyst was not able to affect the reaction. This explains the decreased activity despite the increased amount of catalyst being used compared to the homogeneous SPEEK catalyst. Due to the way the pellets were manufactured, they had small pockets of air trapped in them. Because of this, they floated to the top of the reaction solution. This also decreased their effectiveness.

At the end of the trial, the reaction mixture was cloudy. This cloudiness was caused by small particles of catalyst that had been ground off of the pellets by the action of the stirrer. This grinding reduced the weight of the pellets over the course of trials 3-1 and 3-2. By the end of trial 3-2, 3422 minutes total reaction time, the weight of the catalyst had decreased by 0.15 g. This translated into a loss of 0.71% of the mass of the catalyst.

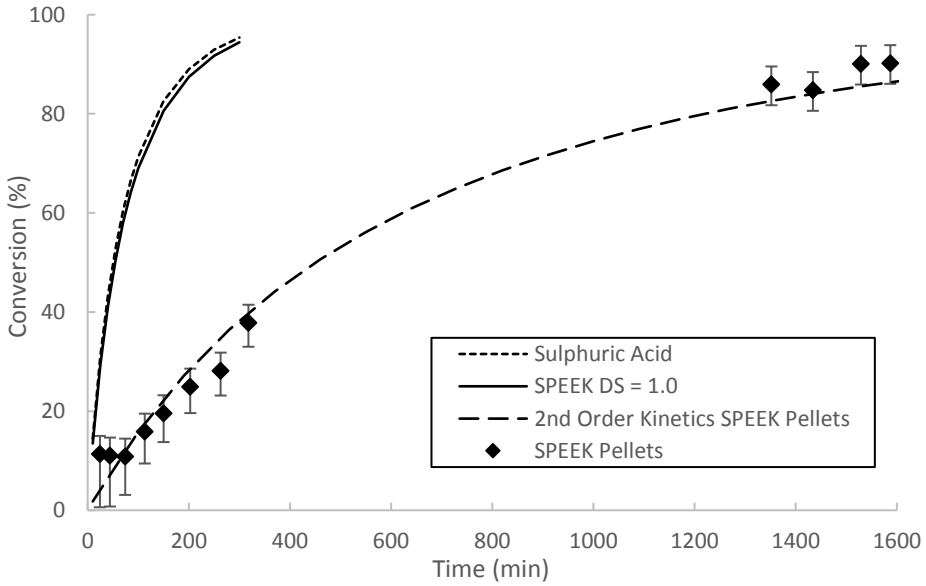

Figure 26: Trial 3-1 –SPEEK pellet catalyzed transesterification of triacetin at 50ºC with a 6:1 methanol:triacetin ratio and 21.05g of catalyst.

4.2.4 Durability of the heterogeneous SPEEK catalyst

Trial series 5 was set up to determine the longevity of the catalyst pellets. Details on the individual trials5-1 to 5-7 can be found in Appendix A: Table 29. All of these trials were carried out at 50°C and had a molar ratio of triacetin:methanol of 1:6. Reactions were run up to 1800 minutes in duration. The total weight of catalyst used at the start of trial 5-1 was 41.44 g. At the end of trial 5-7 the catalyst pellets were dried and weighed again and had a mass of 39.58 g. This loss in weight is due to small pieces being ground off of the larger pellets. This equates to a loss of 4.5% of the catalyst mass over the duration of the seven trials.

Figure 27 shows a graph of the transesterification reaction conversion vs time for trials 5-1 and 5-7. The kinetic constants for these two reactions are $0.90x10^{-3}$ min^{-1} and $0.26x10^{-3}$ min^{-1}. There is a significant drop in activity between the two trials. This has occurred due to loss of catalyst on the surface of the pellets. Because of this loss in surface area, it was not possible to determine if there was any chemical deactivation of the catalyst. Figure 28 shows a magnification of a SPEEK catalyst pellet that had not been used in a reaction. The pellet had gone through the wash cycle to remove any remaining sulphuric acid and was then dried before the photo was taken. The pellet is well textured and displays considerable surface area for the reaction to take place on. In contrast to this, Figure 29 shows a SPEEK catalyst pellet that has undergone 170 hours of reaction time. This pellet has been ground down to a smooth surface. The texture visible on the pellet in Figure 28 no longer exists on the pellet in Figure 29.

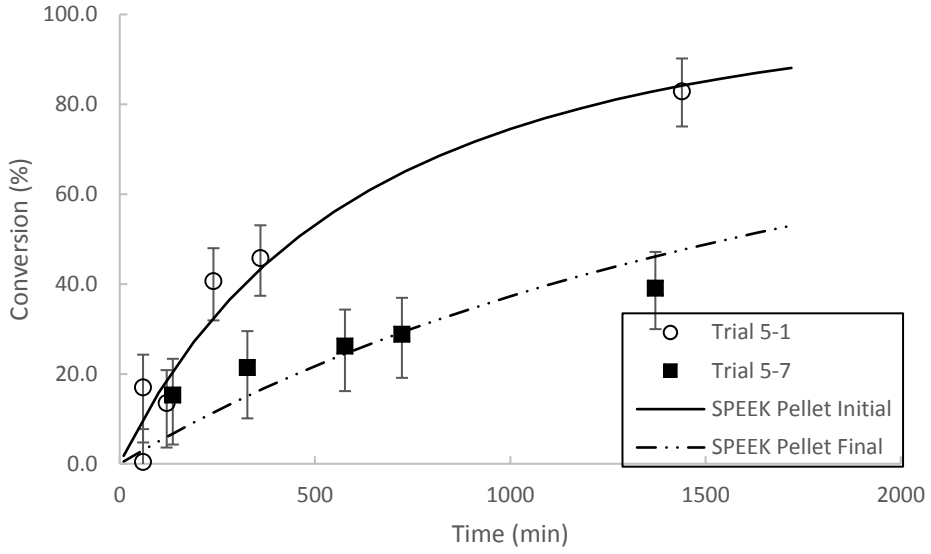

Figure 27: A comparison of the rate of reaction between trial 5-1 and 5-7 using second order kinetics. The transesterification of triacetin in methanol at 50°C.

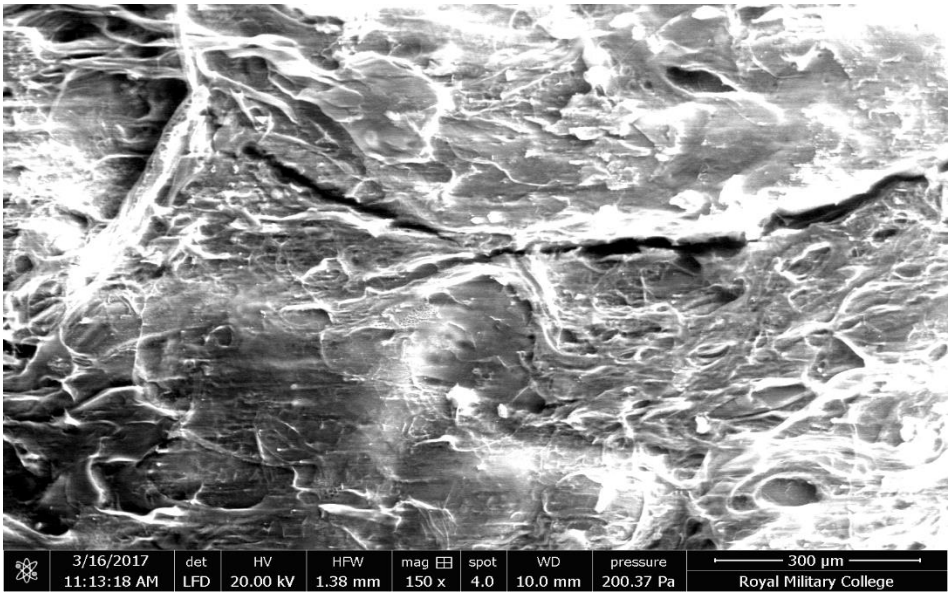

Figure 28: SEM magnification (150x) of a SPEEK catalyst pellet before it was used in a reaction.

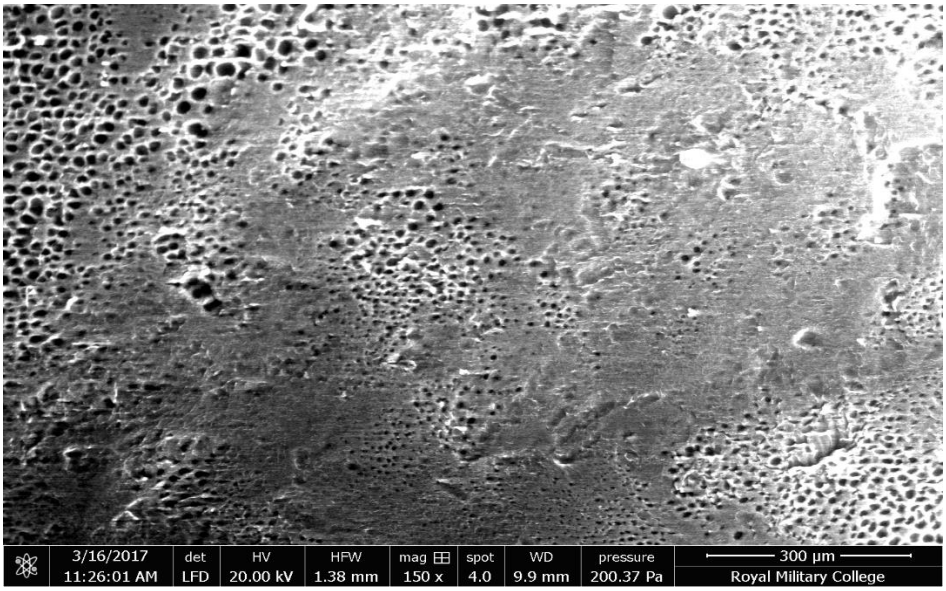

Figure 29: SEM magnification (150x) of a SPEEK catalyst pellet after it has been used in a transesterification reaction for 170 hours.

Furthermore, the pellet in Figure 29 is pockmarked with small holes. These holes, like the loss in texture, indicate that more SPEEK has dissolved in the reactive mixture through repeated transesterification reactions. These pockets of SPEEK that have a higher DS are due to the manufacturing process of the pellet. When the PEEK partially dissolved into concentrated sulphuric acid, it formed a gel. The gel was not homogenous, which would allow pockets of sulphuric acid to react at different rates. Areas with more sulphuric acid reacted quicker than areas with less sulphuric acid. Water produced by the sulphonation reaction in regions of captured sulphuric acid would dilute the sulphuric acid, which slowed the reaction rate in these regions. The methanol rich reactive transesterification solution would slowly dissolved the areas with a high DS creating the pockmarks seen in Figure 29.

The SEM was used to examine a pellet and map its surface for the concentrations of Sulphur. This was done using the EDS system. Figure 30 is a visual photo of the surface area of the pellet. The surface was textured, and had some of the pockmarks described above. The overall DS based off of the EDS elemental count was 0.36. Figure 31 shows the elemental breakdown of what the surface was composed of. The green dots represent carbon, the magenta dots represent oxygen and the yellow dots represent sulphur. The majority of the colour in this photo is green, as is expected. Figure 32 shows just the sulfur component of the surface. This is important because sulfur appears at an active site. When the carbon an oxygen points were removed and just the sulfur points remained, the sulfur was evenly distributed throughout the sample. There are two areas that were less dense, but the resolution of the system was not high enough to determine if there were areas with a much higher DS than the rest of the sample.

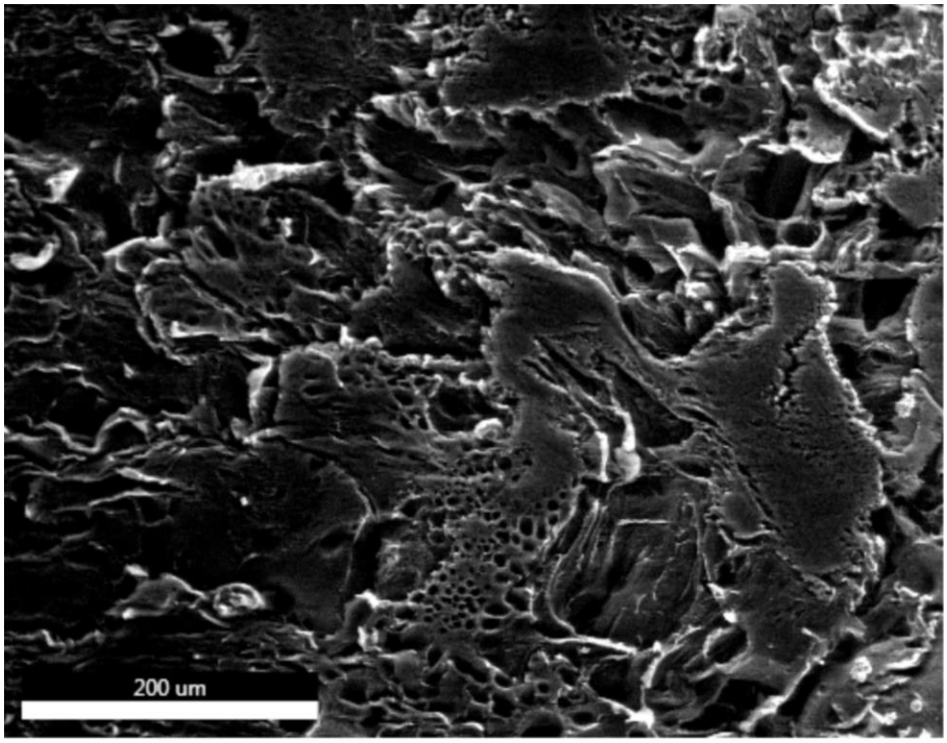

Figure 30: SEM magnification of a catalyst pellet after being washed and before being used in a transesterification reaction.

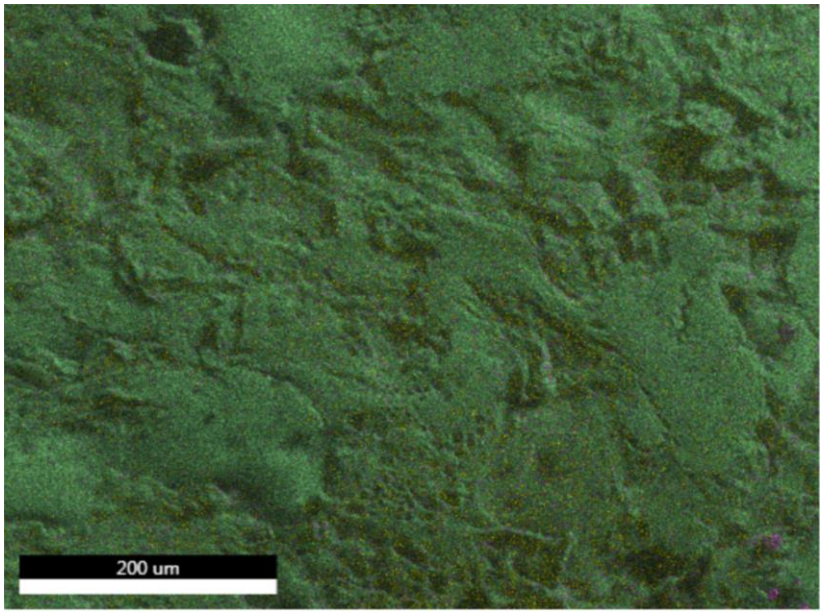

Figure 31: SEM-EDS imaging of a pellet with colour coded elements. Green is carbon, magenta is oxygen and yellow is sulfur.

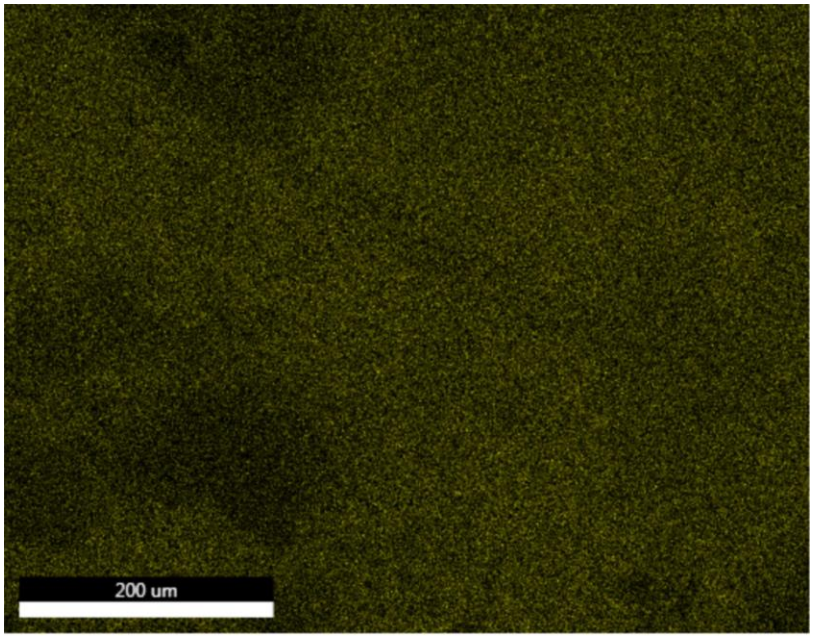

Figure 32: SEM-EDS imaging of a pellet with only the sulfur element being shown.

A similar scan was done using a SPEEK catalyst pellet that had been used in trial 5, and it showed similar results. The sulfur was evenly distributed throughout the sample.

Due to the mechanical degradation of the catalyst, there was no opportunity to determine if there was any chemical fouling of the catalyst. To prevent the mechanical degradation of the catalyst, a new approach must be developed. Some of the ideas for future research include catalyzing the interior of tubes or using stationary coils as catalysts. This would prevent the mechanical degradation that is seen with the current method. Cross-linking of SPEEK would also prevent solvation of SPEEK over extended use as a catalyst.

The SEM results presented in Figure 29 demonstrated that SPEEK was vulnerable to solvation in a methanol-rich reactive mixture, over extended exposure, even at a DS of 0.36. This can be attributed to the mechanical damage exposing pockets of SPEEK that have a higher degree of sulfonation. These pockets are formed when the PEEK partially dissolves into concentrated sulphuric acid. The acid forms pockets that create regions of SPEEK with a higher DS. These pockets can then be solvated by the methanol and methyl acetate in the reaction solution. This leaves the pockmarks that can be seen in Figure 29.

This research work has demonstrated that SPEEK works as an acid catalyst in a transesterification reaction. As a homogeneous catalyst its effectiveness is comparable to sulphuric acid. As a heterogeneous catalyst SPEEK is soft and vulnerable to mechanical degradation.

5 Conclusion

The need for a carbon neutral liquid fuel exists, and biodiesel is a drop in replacement that can be used in existing applications without engine modification. Using a solid acid catalyst to make biodiesel simplifies the process, which reduces costs. One of the most promising solid acid catalyst categories is sulfonated carbon chains. SPEEK is a good candidate for an effective solid acid catalyst.

In order to determine how effective SPEEK is as a catalyst, a two phase experiment was set up. The first phase was to produce SPEEK as a catalyst and the second phase was to determine how effective the catalyst was in a transesterification reaction.

Phase one, producing SPEEK, was broken down into three steps. The first was to determine the sulphonation rate of PEEK as a function of acid concentration, temperature and reaction time. A model was applied using a kinetic equation for sulfonating aromatic rings which was combined with the Arrhenius equation. The activation energy, E_a, and and pre-exponential coefficient,K_0, were calculated to be 18.73 kcal/mol and 1.238×10^{11} L/mol h respectively. These values compared well with those found in literature. The model closely represented the experimental data.

The second step was to examine the solvation rate of PEEK in varying concentrations of sulphuric acid. The solvation rate was found to decrease with a decreasing concentration of sulphuric acid. This was attributed to the fact that SPEEK dissolves quicker into sulphuric acid, and PEEK is sulfonated at slower rates in lower sulphuric acid concentrations.

The final step of phase one was to determine a method to manufacture a catalyst that would not dissolve in a methanol solution. Because SPEEK with a DS over 0.4 will dissolve in boiling methanol, a method was devised to produce catalyst pellets with a core of PEEK and a skin of SPEEK. PEEK pellets were partially sulfonated in sulphuric acid and washed in boiling methanol to remove any chains of SPEEK that were not anchored to the PEEK core. The SPEEK skin on the pellets was determined to have a DS of 0.36 using SEM-EDS.

The second phase of the experiment was to use the SPEEK as a catalyst in transesterification reactions, which was broken down into four steps. The first step examined sulphuric acid as a baseline catalyst in the transesterification reaction. Triacetin was used as the triglyceride for all reactions. 0.5g of sulphuric acid was used as the catalyst. The reaction reached 90% conversion after 200 min.

The second step in the study of transesterification used SPEEK as a homogeneous catalyst. SPEEK with a DS of 1.0 dissolves in methanol. 3.78g of SPEEK with a DS of 1.0 was used to catalyze transesterification reactions. The amount of SPEEK used was equivalent to the same number of acid sites in the reaction using

sulphuric acid as a baseline. When the dissociation of the acids was considered, SPEEK was more active than the sulphuric acid. The non-polar regions on the SPEEK molecule make it a better catalyst for organic reactions. The reactions had a kinetic curve that was almost identical to that of the sulphuric acid. This shows that SPEEK is just as effective as a homogeneous catalyst as sulphuric acid in a transesterification reaction.

The third step in the study of transesterification used a heterogeneous SPEEK catalyst in the form of pellets with a PEEK core. The kinetic constant for the reaction catalyzed by sulphuric acid was 9 times larger than the kinetic constant for the reaction catalyzed by SPEEK pellets. This is due to fewer catalytic sites available for reaction on the pellets. Although the catalyst pellets worked as a heterogeneous catalyst a better design with a higher surface area to mass ratio would increase the reaction rate while minimizing the amount of catalyst required.

The fourth step in the study of transesterification examined the reusability of the catalyst. In this step a batch of SPEEK catalyst pellets were reused for a total of seven runs that lasted around 24 hours each. There was a significant decrease in reactivity over this time. During each run, SPEEK was ground off of the surface of the catalyst pellets. At the end of each run, the reaction solution was cloudy due to fragments of the catalyst being removed from the pellets. Over the course of the reaction 4.5% of the pellet mass was lost but it was the pellet skin that was affected which was confirmed by SEM imaging.

Future research must aim at strengthening the resistance of the SPEEK catalyst against degradation over extended use, or to change the reactor design to minimize damage to the catalyst.

In closing this research is very promising for using SPEEK as an effective catalyst in acid catalyzed transesterification reactions. With further improvements on the strategy to use SPEEK as a heterogeneous catalyst the cost of chemical separation following transesterification could be significantly reduced and be attractive for the large scale production of biodiesel.

6 Future work

This study is the first step to creating an effective heterogeneous acid catalyst using SPEEK. It can be used as a foundation block for further research. Future works can focus on transesterification of long chain triglycerides, catalyst durability and reactor design.

Long chain triglycerides have a low solubility in methanol, which means that the reaction is slowed down by mass transfer between the two phases. Using a homogeneous catalyst introduces another phase into the system. The effect of this must be studied. The benefit of SPEEK is that it absorbs methanol which will keep the methanol readily available for reaction.

There are many methods to improving the durability of the catalyst. One method is to change the form of the catalyst from a pellet to a matrix that will not move during the reaction, like a membrane. Another method is to toughen the outer shell of the catalyst. This could be done by cross linking SPEEK. A reactor design that minimizes the damage to the catalyst can also be investigated.

7 References

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Appendix A: Raw Data.

Table 16: Summary of experiments using 18 molar sulphuric acid as a catalyst

Trial	Catalyst Type	Reaction Time	Catalyst Concentration	Methanol: triacetin Ratio	Temperature (°C) (±2)
1-1	Sulphuric Acid (18 molar)	187 min	0.52 % (by weight)	5.9:1	50
1-2	Sulphuric Acid (18 molar)	200 min	0.52 % (by weight)	6.0:1	50
1-3	Sulphuric Acid (18 molar)	125 min	0.51 % (by weight)	6.2:1	50

Table 17: Integration values and calculated conversions for each sample taken in Trial 1-1

	Trial 1-1-1	Trial 1-1-2	Trial 1-1-3	Trial 1-1-4	Trial 1-1-5	Trial 1-1-6	Trial 1-1-7
Integration Range							
1	28.29	28.38	22.91	21.7	21.78	23.72	20.54
2	8.35	8.82	17.27	18.62	33.53	32.99	34.15
3	38.22	38.5	35.92	36.08	24.66	23.22	24.43
4	25.14	24.31	23.9	23.59	20.03	20.08	20.88
Species Concentration							
Unreacted Chain	7.39	7.17	4.30	3.65	1.58	2.38	1.28
Reacted Chain	3.23	3.60	3.77	3.59	10.94	12.02	10.26
Methanol	12.74	12.83	11.97	12.03	8.22	7.74	8.14
Methyl Acetate	0.99	0.94	3.66	4.21	5.10	4.32	5.68
Conversion(%)	30.4	33.5	46.7	49.6	87.4	83.5	88.9
Time (min)	16	31	48	68	83	103	187

Table 18: Integration values and calculated conversions for each sample taken in Trial 1-2

	Trial 1-2-1	Trial 1-2-2	Trial 1-2-3	Trial 1-2-4	Trial 1-2-5	Trial 1-2-6	Trial 1-2-7	Trial 1-2-8
Integration Range								
1	31.76	30.03	28.07	29.56	30.34	25.46	20.97	23.08
2	0.89	4.12	9.8	13.07	15.68	23.01	31.75	30.8
3	40.06	40.15	37.5	34.49	31.89	30.01	25.99	26.83
4	27.3	25.7	24.64	22.89	22.1	21.51	21.32	19.3
Species Concentration								
Unreacted Chain	9.88	8.54	7.06	6.91	6.80	4.20	1.74	2.09
Reacted Chain	1.94	2.42	3.80	6.55	8.38	8.46	9.40	10.66
Methanol	13.35	13.38	12.50	11.50	10.63	10.00	8.66	8.94
Methyl Acetate	-0.78	0.03	1.15	0.72	0.57	2.97	5.36	4.35
Conversion (%)	16.4	22.1	35.0	48.6	55.2	66.8	84.3	83.6
Time (min)	2	15	30	45	60	90	120	200

Table 19: Integration values and calculated conversions for each sample taken in Trial 1-3

	Trial 1-3-1	Trial 1-3-2	Trial 1-3-3	Trial 1-3-4	Trial 1-3-5	Trial 1-3-6	Trial 1-3-7	Trial 1-3-8
Integration Range								
1	29.96	29.04	27.02	26.69	25.43	24.22	22.44	20.64
2	0	5.14	12.33	13.27	17.6	24.08	32.05	33.82
3	45.69	39.51	36.16	37.35	34.26	30.39	26.54	26.05
4	23.83	26.43	24.47	22.69	22.71	21.3	18.97	19.49
Species Concentration								
Unreacted Chain	8.37	8.26	6.42	5.74	4.93	3.58	1.66	0.97
Reacted Chain	0.77	2.10	4.27	4.68	5.80	8.12	10.83	10.34
Methanol	15.23	13.17	12.05	12.45	11.42	10.13	8.85	8.68
Methyl Acetate	-0.43	0.55	1.74	1.83	2.64	3.52	4.67	5.53
Conversion (%)	8.5	20.3	39.9	44.9	54.1	69.4	86.7	91.4
Time (min)	2	15	30	45	60	90	120	125

Table 20: Summary of reaction conditions using SPEEK with a DS = 1 as a homogeneous catalyst in a transesterification reaction

Trial	Catalyst Type	Reaction Time	Catalyst Concentration	Methanol: triacetin Ratio	Temperature (°C) (±2)
2-1	SPEEK 100%	103 min	3.81 g	5.9:1	50
2-2	SPEEK 100%	128 min	3.78 g	6.0:1	50
2-3	SPEEK 100%	180 min	3.78 g	6.2:1	50

Table 21: Integration values and calculated conversions for each sample taken in Trial 2-1

	Trial 2-1-1	Trial 2-1-2	Trial 2-1-3	Trial 2-1-4	Trial 2-1-5	Trial 2-1-6	Trial 2-1-7	Trial 2-1-8
Integration Range								
1	31.38	29.23	29.02	25.43	25.8	26.67	25.95	27.68
2	1.32	6.68	13.96	19.38	23.56	24.34	27.14	31.42
3	39.13	38.22	33.58	33.05	29.64	27.26	26.09	26.34
4	28.17	25.87	23.45	22.15	21.01	21.72	20.81	14.57
Species Concentration								
Unreacted Chain	9.94	8.08	6.78	4.64	4.15	4.62	3.88	2.54
Reacted Chain	1.78	3.03	6.52	6.68	9.00	9.89	10.78	14.67
Methanol	13.04	12.74	11.19	11.02	9.88	9.09	8.70	8.78
Methyl Acetate	-0.55	0.55	1.03	2.75	2.85	2.62	3.06	2.32
Conversion (%)	15.2	27.3	49.0	59.0	68.4	68.2	73.5	85.3
Time (min)	2	17	33	52	67	81	103	1226

Table 22: Integration values and calculated conversions for each sample taken in Trial 2-2

	Trial 2-2-1	Trial 2-2-2	Trial 2-2-3	Trial 2-2-4	Trial 2-2-5	Trial 2-2-6	Trial 2-2-7	Trial 2-2-8	Trial 2-2-9
Integration Range									
1	30.19	28.57	26.39	22.33	23.44	22.73	22	23.46	26.9
2	2.05	5.2	10.99	16.09	20.04	24.98	26.78	30.2	37.48
3	42.99	42.58	38.61	38.57	32.18	28.75	27.7	24.91	22.78
4	24.76	23.65	23.77	23.01	24.35	23.57	23.56	21.44	12.86
Species Concentration									
Unreacted Chain	8.51	7.34	6.11	3.93	4.41	3.55	3.13	2.86	1.31
Reacted Chain	1.68	2.14	3.33	2.92	5.36	7.23	7.56	10.40	17.13
Methanol	14.33	14.19	12.87	12.86	10.73	9.58	9.23	8.30	7.59
Methyl Acetate	-0.25	0.54	1.81	3.74	3.70	4.31	4.73	4.29	2.98
Conversion (%)	16.5	22.6	35.3	42.6	54.8	67.1	70.7	78.4	92.9
Time (min)	12	27	43	64	76	90	111	128	1000

Table 23: Integration values and calculated conversions for each sample taken in Trial 2-3

	Trial 2-3-1	Trial 2-3-2	Trial 2-3-3	Trial 2-3-4	Trial 2-3-5	Trial 2-3-6	Trial 2-3-7	Trial 2-3-8
Integration Range								
1	33.37	30.08	30.56	28.12	26.39	25.16	23.41	22.67
2	3.43	7.72	13.64	18.35	20.46	23.68	29.29	31.18
3	34.55	35.58	30.07	28.42	29.09	28.72	25.92	25.11
4	28.64	26.62	25.73	25.11	24.06	22.45	21.38	19.5
Species Concentration								
Unreacted Chain	10.67	8.53	8.02	6.55	5.44	4.28	2.89	2.10
Reacted Chain	4.07	4.01	7.18	7.73	7.63	8.45	9.95	10.79
Methanol	11.52	11.86	10.02	9.47	9.70	9.57	8.64	8.37
Methyl Acetate	-1.12	0.35	0.56	1.82	2.58	3.20	4.24	4.40
Conversion (%)	27.6	32.0	47.2	54.1	58.4	66.4	77.5	83.7
Time (min)	15	30	45	60	85	140	180	1000

Table 24: Transesterification reactions using two different batches of SPEEK pellets as a catalyst.

Trial	Catalyst Type	Reaction Time	Catalyst Concentration	Methanol: triacetin Ratio	Temperature (^{o}C) (±2)
3-1	SPEEK Pellets	1587 min	21.05 g	5.8:1	50
3-2	SPEEK Pellets	1835 min	21.05 g	6.1:1	50
4-1	SPEEK Pellets	1607 min	20.67 g	6.0:1	50
4-2	SPEEK Pellets	1500 min	20.67 g	6.0:1	50

Appendix A: Raw Data

Table 25: Integration values and calculated conversions for each sample taken in Trial 3-1

	Trial 3-1-1	Trial 3-1-2	Trial 3-1-3	Trial 3-1-4	Trial 3-1-5	Trial 3-1-6	Trial 3-1-7	Trial 3-1-8	Trial 3-1-9	Trial 3-1-10	Trial 3-1-11	Trial 3-1-12	Trial 3-1-13	Trial 3-1-14
Integration Range														
1	40.11	39.98	39.89	41.98	43.57	45.98	47.5	52.31	64.19	59.72	86.22	84.65	89.63	89.77
2	59.89	60.03	60.11	58.03	56.42	54.01	52.51	47.68	35.81	40.27	14.39	15.34	10.36	10.23
3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Species Concentration														
Unreacted Chain	19.96	20.01	20.04	19.34	18.81	18.00	17.50	15.89	11.94	13.42	4.80	5.11	3.45	3.41
Reacted Chain	2.56	2.49	2.44	3.65	4.58	5.99	6.87	9.68	16.61	14.01	29.33	28.55	31.45	31.53
Methanol	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Methyl Acetate	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Conversion (%)	11.4	11.1	10.8	15.9	19.6	25.0	28.2	37.9	58.2	51.1	85.9	84.8	90.1	90.2
Time (min)	24	44	74	113	150	203	263	318	388	444	1352	1434	1529	1587

Table 26: Integration values and calculated conversions for each sample taken in Trial 3-2

	Trial 3-2-1	Trial 3-2-2	Trial 3-2-3	Trial 3-2-4	Trial 3-2-5	Trial 3-2-6	Trial 3-2-7	Trial 3-2-8	Trial 3-2-9	Trial 3-2-10	Trial 3-2-11
Integration Range											
1	45.2	51.64	53.97	53.65	54.62	53.83	80.49	91.99	89.54	89.07	90.13
2	54.8	48.36	46.04	46.36	45.39	46.17	19.51	8	10.5	10.85	9.88
3	0	0	0	0	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	0	0	0	0
Species Concentration											
Unreacted Chain	18.27	16.12	15.35	15.45	15.13	15.39	6.50	2.67	3.50	3.62	3.29
Reacted Chain	5.53	9.29	10.65	10.46	11.03	10.57	26.12	32.83	31.39	31.14	31.74
Methanol	0	0	0	0	0	0	0	0	0	0	0
Methyl Acetate	0	0	0	0	0	0	0	0	0	0	0
Conversion (%)	23.2	36.6	41.0	40.4	42.2	40.7	80.1	92.5	90.0	89.6	90.6
Time (min)	63	124	243	307	362	417	1398	1484	1549	1748	1835

Table 27: Integration values and calculated conversions for each sample taken in Trial 4-1

	Trial 4-1-1	Trial 4-1-2	Trial 4-1-3	Trial 4-1-4	Trial 4-1-5	Trial 4-1-6	Trial 4-1-7	Trial 4-1-8	Trial 4-1-9	Trial 4-1-10
Integration Range										
1	57.31	65.79	77.09	85.57	86.16	89.67	91.1	91.69	93.07	98.28
2	42.69	34.21	22.91	14.43	13.84	10.33	8.9	8.31	6.93	1.72
3	0	0	0	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	0	0	0
Species Concentration										
Unreacted Chain	14.23	11.40	7.64	4.81	4.61	3.44	2.97	2.77	2.31	0.57
Reacted Chain	12.60	17.54	24.14	29.08	29.43	31.47	32.31	32.65	33.46	36.50
Methanol	0	0	0	0	0	0	0	0	0	0
Methyl Acetate	0	0	0	0	0	0	0	0	0	0
Conversion (%)	47.0	60.6	76.0	85.8	86.4	90.1	91.6	92.2	93.5	98.5
Time (min)	111	259	413	546	672	776	915	1326	1468	1607

Table 28: Integration values and calculated conversions for each sample taken in Trial 4-2

	Trial 4-2-1	Trial 4-2-2	Trial 4-2-3	Trial 4-2-4	Trial 4-2-5	Trial 4-2-6	Trial 4-2-7
Integration Range							
1	42.12	40.51	43.17	48.73	53.92	53.79	56.88
2	57.88	59.49	56.83	51.27	46.08	46.21	43.12
3	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0
Species Concentration							
Unreacted Chain	19.29	19.83	18.94	17.09	15.36	15.40	14.37
Reacted Chain	3.74	2.80	4.35	7.59	10.62	10.54	12.35
Methanol	0	0	0	0	0	0	0
Methyl Acetate	0	0	0	0	0	0	0
Conversion (%)	16.2	12.4	18.7	30.8	40.9	40.6	46.2
Time (min)	131	238	388	503	721	980	1500

Table 29: Transesterification reaction using SPEEK pellets to determine their longevity.

Trial	Catalyst Type	Reaction Time	Catalyst Weight	Methanol: triacetin Ratio	Temperature (^{o}C) (±2)
5-1	SPEEK Pellets	1432 min	41.44 g	6.1:1	50
5-2	SPEEK Pellets	1335 min		6.0:1	50
5-3	SPEEK Pellets	1467 min		5.9:1	50
5-4	SPEEK Pellets	1432 min		5.7:1	50
5-5	SPEEK Pellets	1427 min		6.0:1	50
5-6	SPEEK Pellets	1638 min		6.2:1	50
5-7	SPEEK Pellets	1372 min		6.0:1	50

Table 30: Integration values and calculated conversions for each sample taken in Trial 5-1

	Trial 5-1-1	Trial 5-1-2	Trial 5-1-3	Trial 5-1-4	Trial 5-1-5
Integration Range					
1	28.58	18.99	15.96	24.86	24.71
2	1.4	33.77	9.05	15.87	16.08
3	43.27	22.54	21.55	33.72	33.93
4	26.75	24.71	15.97	25.55	25.29
Species Concentration					
Unreacted Chain	8.47	1.74	3.73	5.60	5.46
Reacted Chain	0.04	8.57	2.56	4.28	4.30
Methanol	14.42	7.51	7.18	11.24	11.31
Methyl Acetate	0.45	6.49	1.59	2.91	2.97
Conversion (%)	0.4	83.1	40.7	43.3	44.1
Time (min)	65	125	248	365	1434

Table 31: Integration values and calculated conversions for each sample taken in Trial 5-2

	Trial 5-2-1	Trial 5-2-2	Trial 5-2-3	Trial 5-2-4	Trial 5-2-5
Integration Range					
1	28.62	27.97	22.89	25.33	21.33
2	5.42	5.19	26.02	16.99	34.25
3	37.76	39.35	24.53	31.23	21.29
4	28.19	27.49	26.55	26.44	23.13
Species Concentration					
Unreacted Chain	8.57	8.14	4.34	5.94	2.18
Reacted Chain	1.76	1.28	7.49	5.02	10.60
Methanol	12.59	13.12	8.18	10.41	7.10
Methyl Acetate	0.83	1.02	4.51	2.87	5.53
Conversion (%)	17.0	13.6	63.3	45.8	82.9
Time (min)	60	120	240	360	1440

Table 32: Integration values and calculated conversions for each sample taken in Trial 5-3

	Trial 5-3-1	Trial 5-3-2	Trial 5-3-3	Trial 5-3-4
Integration Range				
1	26.25	31.21	30.18	29.74
2	5.86	3.68	5.8	6.58
3	42.84	41.47	39.78	40.42
4	23.29	23.05	22.83	23.25
Species Concentration				
Unreacted Chain	6.47	8.37	7.83	7.58
Reacted Chain	1.19	3.44	3.87	3.64
Methanol	14.28	13.82	13.26	13.47
Methyl Acetate	1.29	-0.68	-0.22	0.17
Conversion (%)	15.5	29.1	33.1	32.4
Time (min)	120	240	500	620

Note: Data from Trial 5-4 and 5-5 were lost due to a computer malfunction.

Table 33: Integration values and calculated conversions for each sample taken in Trial 5-6

	Trial 5-6-1	Trial 5-6-1	Trial 5-6-1	Trial 5-6-1	Trial 5-6-1	Trial 5-6-1
Integration Range						
1	27.09	29.46	30.01	27.16	28.92	25.7
2	5.76	3.63	5.35	5.83	11.61	12.81
3	42.36	41.23	42.26	38.43	37.31	35.03
4	23.23	23.6	23.85	21.67	23.44	22.64
Species Concentration						
Unreacted Chain	6.77	7.99	7.80	6.88	6.80	5.75
Reacted Chain	1.70	2.40	2.93	2.88	5.15	4.45
Methanol	14.12	13.74	14.09	12.81	12.44	11.68
Methyl Acetate	0.98	-0.12	0.15	0.34	1.01	1.80
Conversion (%)	20.0	23.1	27.3	29.5	43.1	43.6
Time (min)	135	253	540	685	1378	1638

Table 34: Integration values and calculated conversions for each sample taken in Trial 5-7

	Trial 5-7-1	Trial 5-7-2	Trial 5-7-3	Trial 5-7-4	Trial 5-7-5
Integration Range					
1	28.42	28.16	26.91	26.25	24.28
2	3.95	6.17	7.93	7.06	12.66
3	41.82	40.1	41.79	48.23	38.39
4	25.1	25.57	23.37	18.46	22.26
Species Concentration					
Unreacted Chain	7.84	7.63	6.42	4.91	4.97
Reacted Chain	1.42	2.09	2.29	1.99	3.19
Methanol	13.94	13.37	13.93	16.08	12.80
Methyl Acetate	0.53	0.90	1.37	1.25	2.45
Conversion (%)	15.3	21.5	26.3	28.9	39.1
Time (min)	136	327	577	723	1372

Sources of error for the sulfonation of PEEK

The sources of error when calculating the degree of sulfonation can be broken down into two groups. The first being random error and the second being systematic errors.

The random error associated with the process can be attributed to:

- Slight variations in the concentration of the sulphuric acid reactant
- Variations in the rate of solvation of PEEK into sulphuric acid
- Temperature fluctuations in the reactor
- Deviations in the NMR spectrum processing

The sum of these errors can be calculated by using the confidence limits for a mean using student T-test. The calculated error applies to all of the data points in one run.

$$\mu = \bar{x} \pm \frac{t_r s}{N^{1/2}}$$

Where:

$$s = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(x_i - \bar{x})^2}$$

$(x_i - \bar{x})$ represents the difference between the measured data point and the kinetic model for each data point. The error calculated with these equations will be applied consistently across all of the data points for each run. A level of significance of 0.05 was used in this model.

There are some systematic errors that occur in this process due to the solubility of SPEEK at different DS. SPEEK with a DS under 0.4 will not dissolve in DMSO, which is the solvent used for the NMR. SPEEK with a DS of over 0.9 can dissolve in the water used to wash the sulphuric acid out of the samples that were taken. A washing technique was used to minimize the amount of SPEEK that dissolved, but it is unclear exactly how much could have been washed out with the sulphuric acid.

PEEK takes up to an hour to dissolve in the sulphuric acid, because of this, there is a range of sulfonation in each sample. If this range follows a normal curve, A sample that has an average DS of 0.4 will only have half of the SPEEK dissolve in DMSO. The measured DS for this sample will be higher than the actual DS of the sample. Because of this, the negative error for samples that have a lower DS is greater than the error for samples with a higher conversion. To eliminate this

systematic error, samples with a DS of under 0.5 were discarded as being inaccurate.

To calculate the error for the calculation of activation energy and the kinetic constant, the error from the data points was propagated through the kinetic formula to the linear form of the equation. From there the LINEST function in excel was used to calculate the error for the slope of the trend line running through the experimental data. This error can then be propagated through the equations used to calculate E_a and k_o.

Sources of error for the transesterification of triacetin

The sources of error for the transesterification of triacetin again can be broken down into the random and the systematic errors. The random errors can be attributed to:

- Slight variations in the degree of sulfonation of the homogeneous SPEEK catalyst
- Agitation of the SPEEK catalyst pellets in the reactor
- Un-neutralized samples over reacting.
- Temperature fluctuations in the reactor
- Deviations in the NMR spectrum processing

The error associated with random errors was calculated the same way as the random error was calculated for the sulfonation of PEEK.

There is a source of systematic error in the processing of the transesterification samples. The method used to determine the conversion from the NMR spectrum outlined in paragraph 3.4.5 gives higher conversion results than expected at low conversion. To determine the error associated with this process, a series of samples were examined looking at the methyl groups on the triacetin and methyl acetate on an NMR spectrum. The results can be seen in Figure 33. There is an error or up to 10% conversion at low conversion. This inflation of low conversion results is added to the random error calculated above when showing the error bars for the transesterification results.

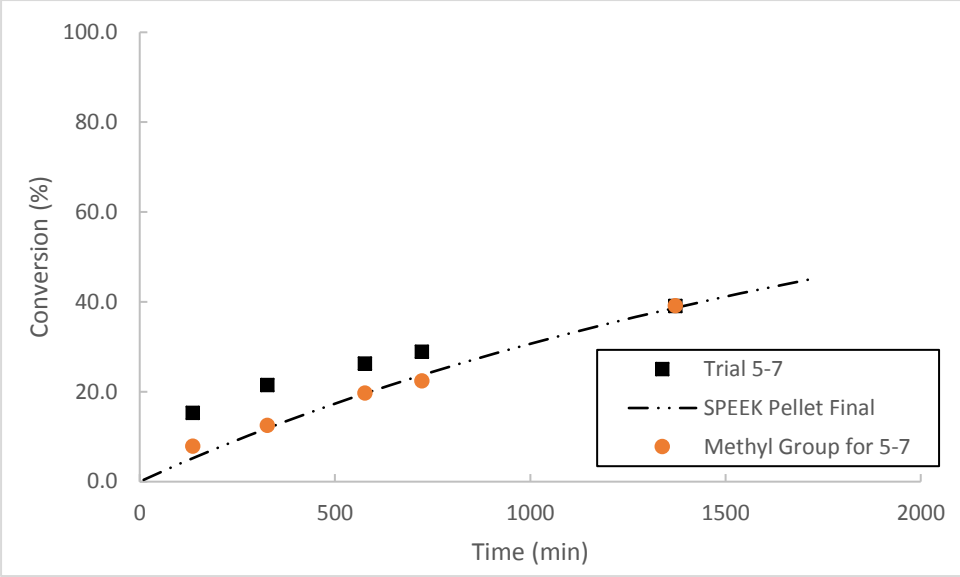

Figure 33: Examining the difference in conversion results using two different methods of calculations based off of an NMR spectrum for trial 5-7.