EVALUATING THE FEASIBILITY OF CONVERTING CRUDE TALL OIL AND TALL OIL FATTY ACIDS INTO BIOFUEL

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DECLARATION

I hereby declare that this dissertation is my own work, unless stated to the contrary in the text, and that it has not been submitted for the degree to any other University or Institution.

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ABSTRACT

The main objective of this study was to evaluate the feasibility of conversion of crude tall oil and tall oil fatty acids into biodiesel. During the Kraft pulping process, Crude Tall Oil originates as tall oil soap, which is separated from recovered black liquor. The soap is then converted to Crude Tall Oil by acidulation with sulphuric acid. The Crude Tall Oil is then fractionated by distillation to produce tall oil fatty acids (TOFA), rosin and pitch.

There were a number of conversional methods that were considered but proved to be inappropriate. A base-catalyzed method was inappropriate with due to the high free fatty acid content on the feedstock, and the acid-base catalyzed method was inappropriate due to the long reaction times and large excess of methanol required. An enzyme based conversion method was also found to be inappropriate because of the high price attached to the purchasing of the enzymes and the stability of the enzyme. A procedure of choice was the supercritical methanol treatment, due to the fact that it requires no separate catalyst.

A procedure was developed for both the feedstocks (i.e. crude tall oil and tall oil fatty acids) using the supercritical methanol treatment. In supercritical methanol treatment, feedstock and methanol were charged to a reactor and were subjected to temperatures and pressures beyond the critical point of methanol (T_c = 240 °C, P_c = 35 bar). The maximum biodiesel yield obtained from Crude tall oil was 66% and was 81% for the tall oil fatty acids that was produced in a single stage process. The temperature and methanol to feedstock ratio effects was also found to yield a maximum biodiesel yield at 325°C and 40:1 respectively. A 20 minutes reaction time was found to be appropriate for the maximum yield of biodiesel.

The final biodiesel produced was also evaluated against a commercial biodiesel product and its parameters measured. The biodiesel resulting from the tall oil fatty acid yielded parameters that were acceptable according to ASTM D6751 specifications for biodiesel. The biodiesel produced from the crude tall oil did not meet the ASTM D6751

specification, and this was mostly attributed to the presence of unsaponifiables which hindered the conversion of oil into biodiesel.

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DEFINITION OF TERMS

Biodiesel – a non-petroleum based alternative diesel fuel that consists of alkyl esters derived from renewable feedstocks such as plant oils and animal fats

Biodegradability – capability of a substance to be decomposed by biological agents such as bacteria

Toxicity – capability of a substance to cause disease when introduced into body tissues of an organism

Cetane number – is an indication of a fuels readiness to auto ignite after it has been injected into the diesel engine.

Flash point – the lowest temperature of a fuel at which it can form an ignitable mixture with air

Transesterification – the reaction between an ester (e.g. triglyceride) and an alcohol (e.g. methanol) to form a new ester (e.g. methyl ester)

Esterification – the reaction between an acid (i.e. free fatty acids) and an alcohol (i.e. methanol) to form an ester (i.e. methyl ester)

Triglyceride – a naturally occurring ester of three fatty acids and glycerol that is the chief constituent of fats and oils

Free fatty acids – a carboxylic acid with a long unbranched aliphatic tail (chain)

Saponification – the reaction between an ester and a base producing alcohol and a salt

Hydrolysis – the decomposition of a substance by a reaction with water

Viscosity – a substance’s resistance to flow

Cloud point – the temperature of a liquid substance at which waxy crystals begin to form causing a cloudy appearance

CHAPTER 1

INTRODUCTION

1.1 Overview of the pulp and paper industry in South Africa

South Africa and Swaziland are the only African producers of pulp and paper (www.pulpandpaper.org). The main raw materials for the industry are mostly found in the equatorial climate in the provinces of Kwazulu-Natal and Mpumalanga. South Africa produces approximately 370,000 tons of mechanical wood pulp, 1,500,000 tons of chemical wood pulp, 316,000 tons of newsprint, 970,000 tons of printing and writing paper and more than one million tons of other paper and paperboard each year (De Bruyn, 2008).

South Africa’s two main pulp and paper companies are **Sappi**, which is listed on the London, Paris and Johannesburg Stock Exchanges, and **Mondi**, which forms part of the Anglo American Industrial Corporation. There is also Nampak and Kimberley Clark. **Nampak** is the Africa’s largest packaging company which offers paper, glass, metal and plastic. **Kimberley Clark**, which is a well-known global brands that provides solutions to enhance health, hygiene and well-being. There are also a number of smaller independents paper and tissue producers, which includes Correll Tissue, Rafalo Paper, Gayatri Paper, South African Paper Mills, Hygienic Tissue, and Status Paper.

Downstream packaging companies include Nampak, Kohler and its subsidiary Carlton Paper, and Consol, which together share more than 80% of the market. Hortors, Bowler Metcalf, Aries, Alex White, Harwill, Clegg, Plastall, Rheem, Transpaco and Coates Brothers are other local operatives while Swedish company Ekman Liebig established a South African presence in late 1995. Mondi and the Dutch group KNP BT have restructured their paper chanting interests in South African companies Paperlink and Fin wood. Between them, Nampak and Carlton Paper control 70% of the SA tissue industry. Nampak's factories at Klip River and Cape Town produce 50 000 tons/year. Carlton Paper produces 47 000 t/year (Sammons and Flynn, 2008).

Operating profit margins for the major pulp and paper producers in South Africa fell from 7.8% in 2008 to 5.9% in 2009 (Mncube, 2010). The profitability of South African pulp and paper industry have traditionally been 5% higher than overseas making it a very lucrative $US 2,5 billion market. Sappi Group reported net debt reduction of US$2.2 billion to US2.1 billion. However the drop in world prices due to the reduction in product demand towards the end of 2007 caused a downturn in profitability (Labuschagne, 2010)

1.1.2 Sappi Paper

Sappi Paper was founded and incorporated in South Africa in 1936. In 1991 Sappi Global expansion began and is, today, a global paper and pulp group. Below is a schematic representation of the different divisions within the Sappi Group.

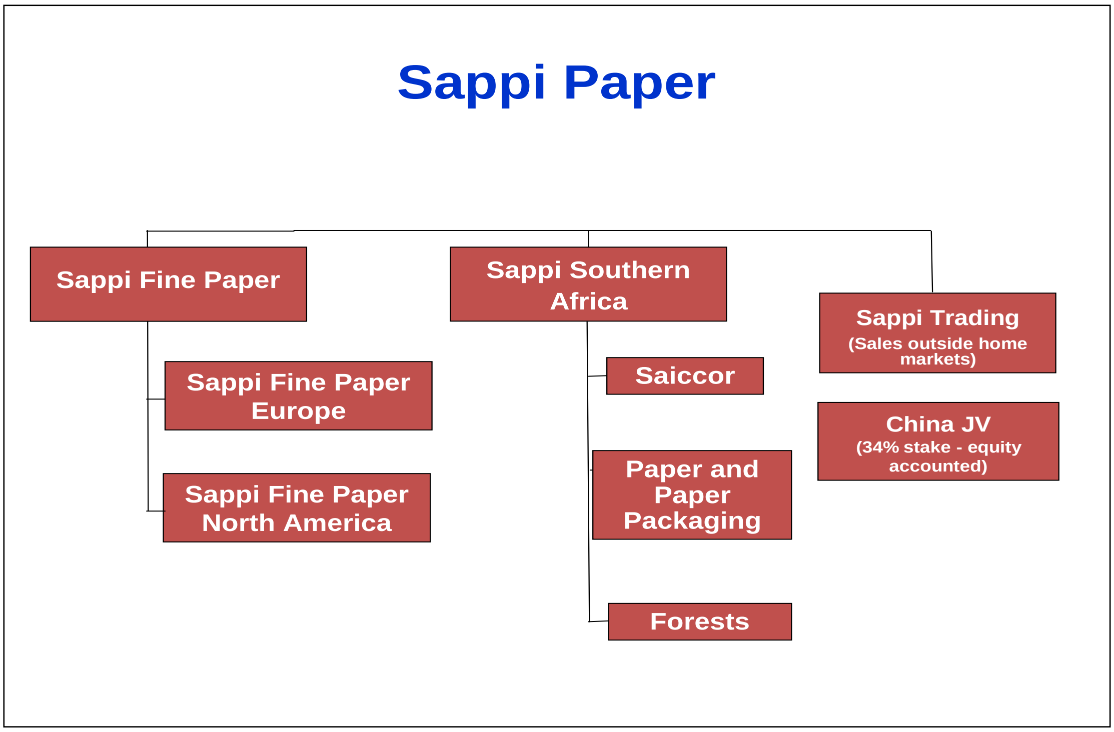


Figure 1.1 Schematic representation of the Sappi Group

Sappi Group is a leading producer of coated fine paper that is widely used in books, brochures, magazines, catalogues and many other print applications. It is also the world’s largest producer of chemical cellulose, used primarily in the manufacture of viscose fibre, acetate tow and consumer and pharmaceutical products. In addition, it produces newsprint, uncoated graphic and business papers, premium quality packaging papers, a range of coated speciality papers and a range of paper grade pulp.

Sappi Group produces 9.5 million tons of different paper grades per annum and has manufacturing operations on four continents. The group has 16, 400 employees worldwide and is selling paper in over 600 countries (Mncube, 2009).

1.1.3 Need to improve economics

Just like many other industries in South Africa and in the world, Sappi Kraft was affected by the global economic recession that took place between the years 2007 to 2010. The global recession had a profoundly negative impact on most sectors of the South African economy as well as the world. It was the recession that extended beyond national borders and affected the global economy. A technical recession definition for a country is two consecutive quarters of negative economic growth as measured by a country's gross domestic product (Higgins and Schall, 2001).

The following is a generic illustration of the impact of global economic recession to Sappi Limited (Boettger, 2010).

- Operating profit of US$33 million excluding special items, special items amounted to a net pre-tax charge of US$106 million compared to US$175million in 2008;
- Sales down 8% to US$5.4 billion;
- Basic EPS loss of 37 US cents;
- Net debt of US$2.6 billion, up US$171 million; and
- No dividend declared.

Based on the above, there was, therefore a need to review the entire papermaking process with the view of establishing if they could be ways of generating extra income within the process. This process also involved looking at the current products as well as the by-products.

This research will look at Crude Tall Oil (CTO), a by-product of the papermaking process and evaluate the feasibility of converting it into bio-diesel. Due to the nature of the papermaking process and the cooking additives that are added into the digester, crude tall oil is a by-product that is unique to Sappi Tugela. No other pulp and paper Mill in the continent of Africa has this by-product.

1.2 Byproducts

1.2.1 Process description

Paper has traditionally been defined as a felted sheet formed on a fine screen from a water suspension of fibers (Smook, 1992). A papermaking process consists of two inter-related processes i.e. pulp mill and paper mill. A pulp mill is a manufacturing facility that converts wood chips or other plant fibre source into a thick fibre board. Depending on the location of the paper mill, this pulp board is then transported for further processing to finally produce paper. The finished product is either bleached or non-bleached, depending on the customer's requirements.

Wood and other plant materials used to make pulp contain three main components (apart from water): cellulose fibres (desired for papermaking), lignin (a three-dimensional polymer that binds the cellulose fibres together) and hemicelluloses, (shorter branched carbohydrate polymers). The aim of pulping is to break down the bulk structure of the fibre source, be it chips, stems or other plant parts, into the constituent fibres.

1.2.2 Types of by-products

There are a number of by-products that are being generated during the pulp and paper making process at Sappi Tugela. Below is the list of those products and their uses:-

- **Sodium lignosulphonate** – currently being sold as a cement additive and developmental work is underway with the Department of Transport to use the product as a dust suppressor.
- **Crude tall oil** – sold to the third party who fractionates it to three components i.e. free fatty acids, rosin and pitch

- **Boiler ash** – sold to the local brick and block manufacturers
- **Secondary fibre –** sold to the third party to make egg-boxes. Development work is also underway for other uses.
- **Cull paper –** sold to the third party to make boxes
- **Turpentine –** Developmental work is underway to find the market for the product

The focus for the study will be on crude tall oil (CTO). The study will look at converting both crude tall oil and tall oil fatty acid as a feedstock for conversion into biodiesel.

1.2.3 Crude Tall Oil and Tall Oil Fatty Acids

Crude tall oil (CTO) is a viscous yellow-black odorous liquid obtained as a by-product of the Kraft process of wood pulp manufacture. It is a major chemical by-product of the Kraft pulp industry processing pinewood for pulp and paper. Crude tall oil starts as tall oil soap separated from recovered black liquor in the Kraft pulping process. The tall oil soap is acidified with H_2SO_4 at 117°c for 1 hour and allowed to separate, to yield crude tall oil. Gullichsen and Paulapuro (2000) listed the components of crude tall oil as follows:-

- 44-55% tall oil fatty acids such as oleic and linoleic acids;
- 25 -35 rosin such as resin acids and other natural matter; and
- 10% pitch

Tall oil fatty acids are used in vehicle paints, soaps/detergents, printing inks, foam inhibition agents, lubricants, greases, flotation agents and industrial oils. **Tall oil rosin** has traditionally been used as a paper size, but this use is declining. Other applications include alkyd resins, printing inks, adhesives, emulsifiers, paint and lacquer for vehicles and soaps. **Tall oil pitch** has certain special applications as an asphalt additive and in rust protection, printing inks and oil-well drilling muds, but its primary use is still as a sulphur-free fuel (Smook, 1997).

1.2.4 Quantities of crude tall oil

The graph below indicates the quantities of crude tall oil production from the financial period of 2007 to 2009.

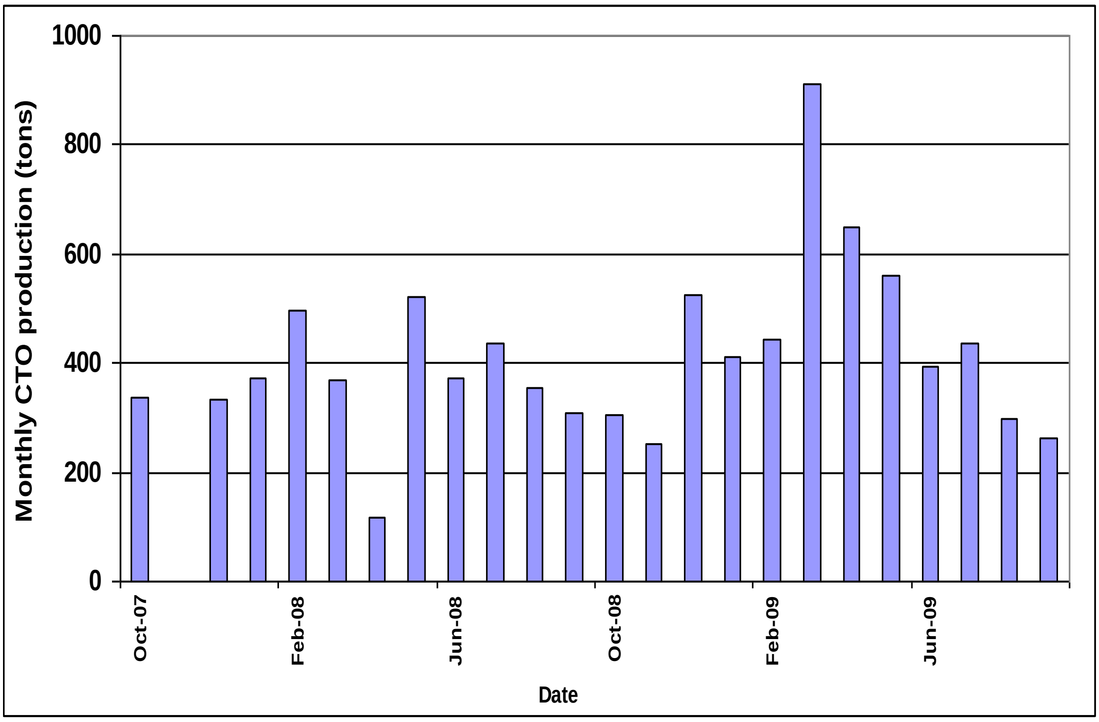


Figure 1.2 – Monthly CTO production

It can be observed that the average production of crude tall oil is 400 tons/month. This tonnage represented significant revenue for the Mill – almost R 12 mil/annum as the product is sold to the third party.

The preliminary research on the potential income that is likely to be generated if the product is converted to biodiesel was R 35 mil/annum (Murray, 2007).

It, therefore, became paramount that the research be under-taken as it has a potential to make a significant improvement in the financial performance of the Mill as well as of the entire Sappi Group.

1.2.5 Biofuel

Humanity's dependence on petroleum for transportation fuel comes at a high cost. The environmental impact of fossil fuels is well documented and known. They contribute to global warming by transferring previously sequestered carbon molecules into the atmosphere as carbon dioxide which is a greenhouse gas (Knothe, 2001). They are also a major source of air pollution through other combustion products found in the exhaust systems of vehicles (Hirsch, 2005). In addition to environmental negatives, the nations that cannot supply their own petroleum needs are forced into an unfavourable balance of payments with petroleum exporters.

Biofuels offer a partial solution to many of these problems mentioned above. It has been claimed that biofuels do not contribute to global warming (Brown, 2003). Like petroleum, exhaust fumes from biofuels contain carbon dioxide. Since plants remove carbon dioxide from the atmosphere during photosynthesis, the net production of CO_2 is arguably zero (Mittelbach and Remschmidt, 2005). The levels of other pollutants are also generally lower with biofuels than with petroleum. The fuel stocks for biofuels are produced by domestic agriculture, which means that biofuels production occurs domestically as well.

Biodiesel is a diesel fuel substitute produced from renewable sources such as vegetable oils, animal fats, and recycled cooking oils. Chemically, it is defined as the mono alkyl esters derived from renewable sources (Friedrick, 2003). Biodiesel is typically produced through the reaction of a vegetable oil or animal fat with methanol or ethanol in the presence of a catalyst to yield glycerine and biodiesel - chemically called methyl or ethyl esters (Biodiesel Education, 2006). These oils are expensive and they generally account for 60 – 80% of the total cost of biodiesel production (Mittelbach and Remschmidt, 2005). The fluctuating price of crude oil provokes the need for the other source of fuel globally.

1.3 Justification for the study

1.3.1 Previous studies

There are a number of studies that relate to biodiesel production that have been conducted and published. Most of them have used spent cooking oil and vegetable oil as feedstocks. These were conventionally converted with much success because of the level of fatty acids present in the feedstock (Balat, 2005).

There is also a study conducted by Schulte in 2007, where he looked at converting both the chicken fat and crude tall oil into biodiesel. The two feedstocks were studied individually as well as a blend. He considered conventional base and acid catalysed procedures and found them to be inappropriate for his study, due to the high fatty acid content within the feedstocks. He then found supercritical methanol treatment as a method of choice.

The results from his study indicated that chicken fat and crude tall oil from Canada can be converted to biodiesel successful. The yields that were achieved for this study were 89 and 94% respectively. He also concluded that the two feedstocks could not be converted as a blend due to the excessive methanol that was required for the reaction.

The properties of the biodiesel produced from study were acceptable by the ASTM D6751 standard which is a requirement that is set-up by a control body for the diesel engines in Canada.

1.3.2 Crude tall oil composition

The graph below indicates the variations of the crude tall oil composition across different regions.

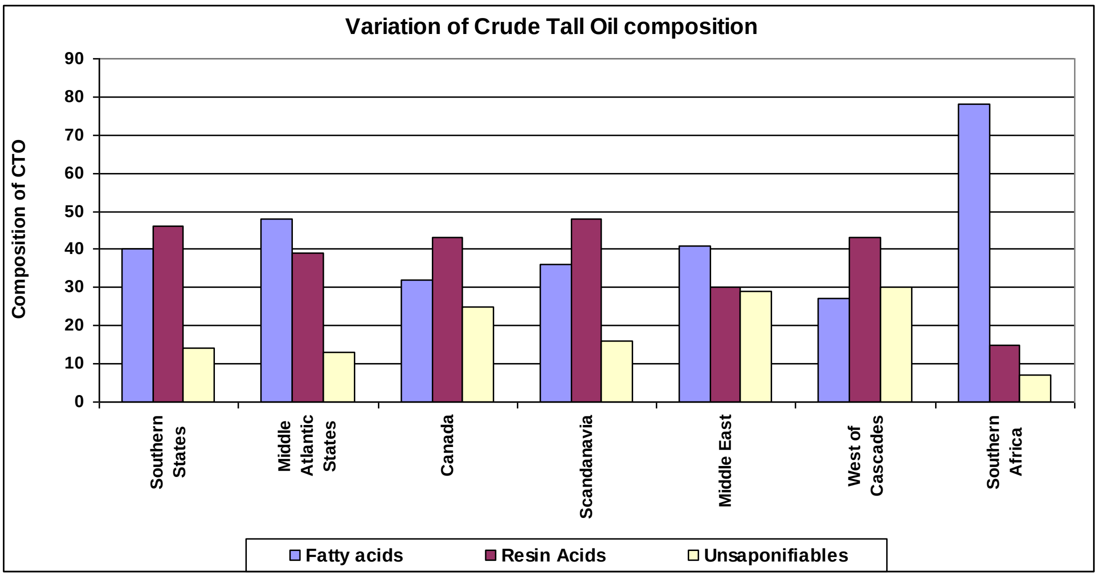


Figure 1.3 – Variation of crude tall oil composition

It can be observed from the figure above that the composition of the Southern African's crude tall oil is significantly different to the other regions that are the dominants suppliers of crude tall oil in the world. This could be attributed to the weather and geographical condition in the different countries.

1.3.3 Purpose of this study

It was therefore important to evaluate the feasibility of converting Southern African's crude tall oil into biodiesel. This was critical to establish and determine the effect of the higher free fatty acids and the lower unsaponifiable that are prevalent from the crude tall oil in the Southern Africa if compared with the product from the other countries. Also, the South African Engine Manufacturers' Association, which is an approving body for the biodiesel that is used in engines, needed to ascertain whether the biodiesel produced from the Southern African crude tall oil will meet the specification set out by the Department of Energy and Minerals (specification attached as Appendix 1).

Also, to address the financial challenges that Tugela Mill finds itself in currently, it is necessary to consider the possible revenue generating streams and quantify their viability.

CHAPTER 2

OBJECTIVE AND APPROACH

2.1 Objective

The overall objective of this study was to evaluate the feasibility of converting of crude tall oil and tall oil fatty acids into biodiesel.

The specific objectives of the study were to:-

- Develop criteria for selecting the best procedure for converting crude tall oil and tall oil fatty acids into biodiesel;
- Select the most suitable procedure for investigation;
- Evaluate the effects of important parameters on the final biodiesel yield and quality;
- Test the final biodiesel product produced from both the feedstock and compare it to SANS 1935 Automotive diesel fuel standard; and
- Perform an economic evaluation.

2.2 Approach and Thesis Organization

Chapter one gives an overview of the pulp and paper industry in South African and the need for this study.

Chapter two provides the objective and approach of the study.

Chapter three is the literature survey on both crude tall oil and biodiesel.

Chapter four discusses the selection of a conversion procedure that was chosen for the investigation

Chapter five describes the apparatus and the protocol that was followed during the study

Chapter six presents and discusses the results that were obtained during the study

Chapter **seven** discusses the overall economic consideration

Chapter **eight** concludes the findings and presents some recommendations.

CHAPTER 3

LITERATURE REVIEW

3.1 Introduction

The literature reviews will cover the three important aspect of the study. The first aspect of the study is the basic pulp and paper process, with the emphasis on the papermaking processes and the crude tall oil chemistry.

The second aspect of the study will look at generic conversion procedures for the spent oil and the specific processes that were considered for the study.

The third aspect will be on biodiesel. In this section, the advantages and disadvantages of using biodiesel will be discussed. The important parameters that are stipulated by the Engine Manufacturers Association for the biodiesel to be suitable for use in the cars will also be discussed.

3.2 Basic papermaking process

(Standard Operating Procedure and the Operator's Manual from Sappi Tugela were used during the basic papermaking process description, unless otherwise stated).

Papermaking process can be divided into 5 interrelated phases i.e. forestry, wood preparation, pulp preparation, paper formation and paper finish. Below is a simplified flow diagram for the integrated pulp and paper mill.

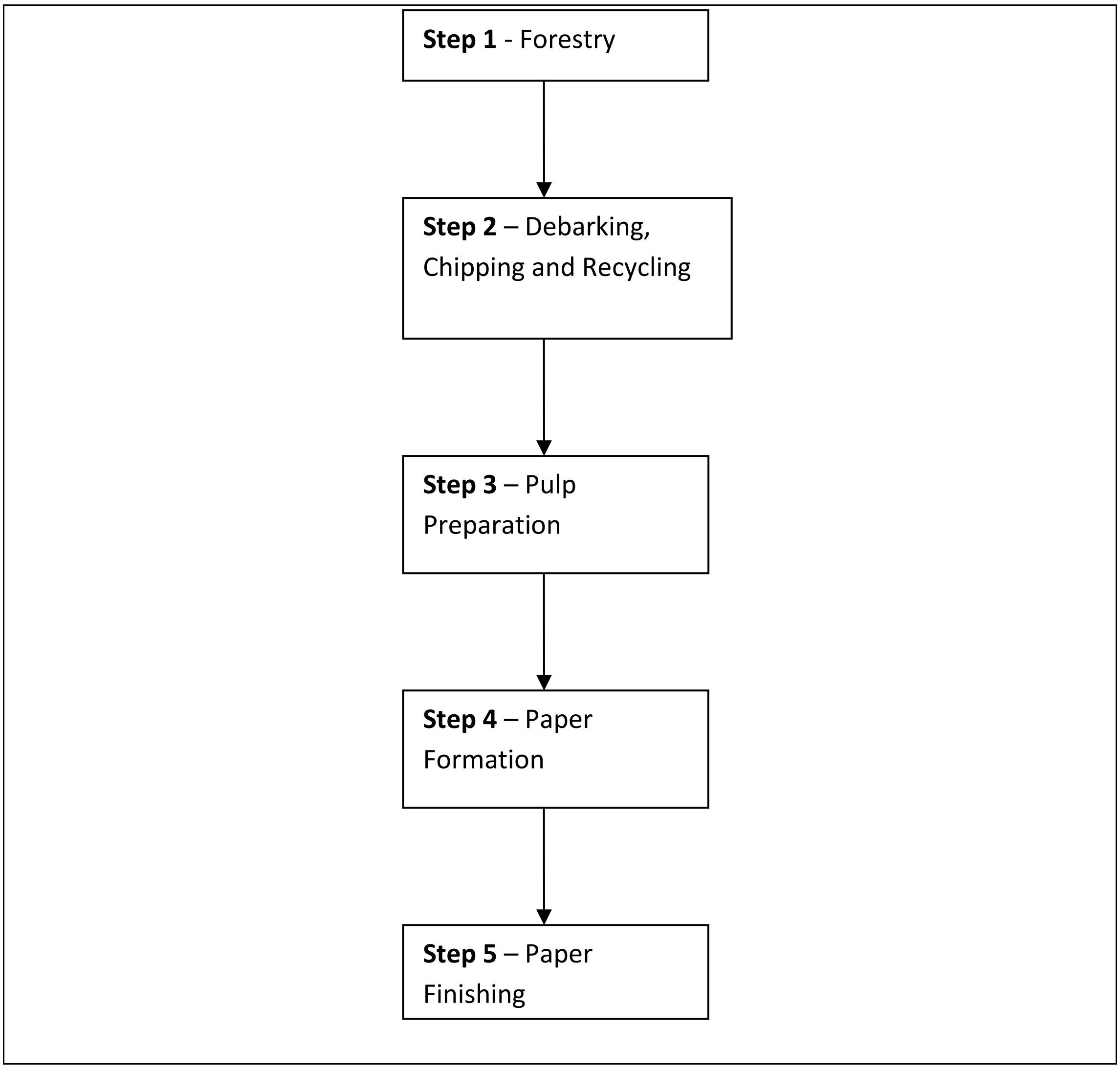


Figure 3.1 – flow diagram for a basic pulp and paper making

3.2.1 Forestry

This process involves growing and harvesting trees according to the required final product specification. Paper producing entities and companies have separate forestry operations that are independently run by competent personnel. After a specified growing period, normally 16 – 18 years, trees are harvested and transported to the paper mills for further processing.

The types of trees used for papermaking can be divided into two major categories i.e. hardwoods and softwoods which are the main sources of wood fibres in South Africa. Hardwood (eucalyptus) generally lose their leaves in autumn, softwoods (pine) are usually evergreen.

Softwood fibres are longer, larger in diameter and have a higher density while hardwood fibres are shorter, smaller in diameter and a lower density. The yield of pulp per unit volume of wood is usually directly related to density. A high wood density generally indicates a slower beating response, lower tensile, burst and fold strength, greater bulk and higher tear strength (Smook, 1992).

Generally, hardwood contains a larger proportion of holocellulose and less lignin as compared to softwoods, but a greater percentage of extractives (Harshaw, 2000).

3.2.2 Wood Preparation

Wood preparation consists of a series of operations which convert the wood into a form suitable for the subsequent pulping operations. In most cases, the ultimate product is wood chips.

Wood is unloaded from a truck or railcar by a front-end loader or by an overhead travelling crane. This process involves transportation in slasher deck, where the logs are sorted and cut into manageable lengths, followed by debarking, chipping, chip screening, and conveyance to storage. Chips are usually stored in outside piles.

3.2.2.1 Debarking

The loading deck is the first element of a log handling operation. The logs are aligned and transported onto sorting and/or slashing and then to debarking system. Log debarking is necessary to ensure that the pulp is free of bark and dirt. Mechanical and hydraulic debarking are the most commonly used bark removing methods. In the mechanical debarking, bark is removed from the logs by friction created from the rotating drum action as the logs rub against each other. In the hydraulic debarking, bark is removed by directing high pressure jets of water against the log. Bark removal is efficient and wood losses are usually under 2% with this method, but the effluent generated is difficult to clean up and the pollution problems have caused many mills to switch from hydraulic to mechanical barkers.

3.2.2.2 Chipping

After debarking, the logs are reduced to chip fragments suitable for the subsequent pulping operations. Flywheel-type disc are the most common chippers used in the industry. The ideal chip size is usually considered to be about 20mm long, and about 4 mm thick, but all chips 10 to 30 mm long and 2 to 5 mm thick are prime materials for pulping. Off-size chips adversely affect the processing and quality of pulp.

3.2.2.3 Chip Screening

Acceptable size chips are usually isolated from fines and oversized pieces by passing the chips over multi-stage vibratory screens. The oversized chips are rejected to a conveyor, which carries them to a “rechipper” usually hammermill that crushes the chips into smaller fractions. The fines are usually burned with the bark.

3.2.2.4 Chip storage

Chip storage is widely utilized primarily because chips are more economical to handle than logs. Outside chip storage is the most common chip storage method, because large inventories of chips can be stored. There are some disadvantages with this method e.g. blowing of fines, air-bone contamination. It is always advisable to provide a ground barrier of concrete or asphalt before building a chip pile to reduce dirt contamination and inhibit any micro-organisms attack on the chip pile. Chip should be stored on a first-in/first-out basis to avoid infection of fresh chips by old chips.

Optimum chip handling depends partly on pulping requirements. Since loss of extractives is high for the first two months of outside storage, all chips for sulphite pulping should go to storage. If by-product recovery is important, then fresh chips should bypass storage wherever possible to maximise yield.

3.2.3 Pulping/cooking Process

Pulping process is the means to rupturing the bonds within the wood structure (Smook, 1992). The task can be accomplished mechanically, thermally, chemically or by combination of these methods.

3.2.3.1 Mechanical Pulping

Mechanical pulping is a process whereby wood is subjected to roughened stone grounding which revolves at a speeds of 1000 to 1200 m/min. Fibres are torn out of the wood, abraded, and removed from the surface of the stone with water. The fibres which have form a low consistency by now are screened to get rid of slivers and other undersize and oversize material, and the consistency of the slurry is increased by removing the water to prepare the stock for papermaking process.

This pulping process have not had much success because of the energy requirements, though the high yield of 95% of conversion from wood into chips have been recorded in some pulp Mills. Also, the paper that is formed from Mechanical pulp is weak, highly opaque which is an advantage to the printers but it tends to discolour, if is exposed to light (Smook, 1992).

Mechanical pulps are most often produced from softwood sources. The smaller, thinner hardwood fibres are more severely damaged during mechanical pulping and yield a finer, more flour-like material that forms an exceedingly weal sheet. Some hardwoods produce an exceptionally bright pulp that is sometimes blended with softwood mechanical pulp to improve optical properties (Janse and Ottisch, 2005).

3.2.3.2 Chemical Pulping

Chemical Pulping is also another pulping process that is widely used in the industry. This process is successful in degrading, dissolving and removing the lignin away from cellulose and hemicellulose by means of chemical reactions. Table 3.1 gives a brief description of different chemical pulping processes and the additives that are utilized in this process.

Lignin is the glue-type material that binds the hemicellulose and cellulose material within the tree structure. Cellulose and hemicellulose is the material that is required to produce paper. However, the yield on this process is around 40 – 50%, and this can be attributed to the vigorous cooking that takes place in the cooking equipment – digester.

During the chemical pulping process, wood chips are subjected to higher temperatures and pressures in a solution of pre-determined cooking additives concentration. The most common cooking processes in the industry are Alkaline and Acidic processes. During the Alkaline process, wood chips are cooked in a solution of NaOH (sodium hydroxide) and Na_2S (sodium sulphide). The lignin is broken down by the alkaline attack into segments and is processes as either sodium or calcium lignosulphonate at the Copeland reactor. In general, paper produced from the alkaline process is normally stronger than the paper produced from other pulping processes.

In the Sulphite process, a mixture sulphurous acid (H_2SO_3) and bi-sulphite ion (HSO_3^-) attacks and solubilises the lignin molecule. The mechanism of this chemical attack removes the lignin while the structure of the molecule remains intact. Depending on the cooking regime, the base for the chemical cooking additive can either be calcium, sodium, magnesium or ionic. Sulphite cooking process can be performed at a wide range of pH values. Sulphurous acid is used for acid sulphite at a pH range of between 1 – 2, and bi-sulphite cooking is carried out at a pH range of between 3 – 5.

Pulp produced from the Sulphite process tends to be lighter in colour compared to Alkaline pulps, and is also easier to bleach, but the paper sheets are weaker than equivalent Kraft sheets. The Sulphite process works well for such softwoods a spruce, fir and hemlock and such hardwood as eucalyptus, but resinous softwood and tannin-containing hardwoods are more difficult to handle. This sensitivity to wood species, along with the weaker pulp strength and the greater difficulty in chemical recovery, are the major reasons for the decline of sulphite process relative to Kraft (Schlebusch, 2007). The trend towards whole tree chipping puts sulfite at a further disadvantage because of its intolerance to bark.

3.2.3.3 Semi-chemical Pulping

This process combines both chemical and mechanical methods. Essentially, the wood chips are partially softened or digested with additives, and the remainder of the pulping action is supplied mechanically, most often in disc refiners. Semi-chemical encompasses the entire intermediate range of pulp yields between pure mechanical and pure chemical pulping i.e. 55 to 90% on dry wood.

The neutral sulphite process (NSSC), is the most widely used semi-chemical process. This process utilizes sodium sulfite cooking liquor which is buffered with sodium carbonate to neutralize the organic acids liberated from the wood during cooking. Spent liquors from semi-chemical pulping operations cannot be discharged directly into receiving waters because of high chemical losses and pollution loads. Processing of spent liquors can be readily accomplished in cross- recovery with an existing Kraft or sulfite mill recovery system. Where cross recovery is not possible, fluidized bed incineration is the most common method used for disposal and recovery.

The table below represents the major chemical and semi-chemical pulping methods.

	Kraft	**Acid Sulphite**	**Bisulphite**	**NSSC**
Chemicals	NaOH and Na_2S	$H2SO_3$ $M(HSO_3)$	$M(HSO_3)$	Na_2SO_3 Na_2CO_3
Cooking Time (hours)	2 - 4	4 - 20	2 - 4	¼ - 1
Liquor pH	13+	1 - 2	3 - 5	7 -9
Cooking Temp	170 – 180°C	120 – 135°C	140 – 160°C	160 – 180°C

Table 3.1 – Major chemical and semi-chemical pulping methods

3.2.4 Cooking Equipment

The overall objective of the pulp mill is to produce quality pulp slurry at the lowest cost while meeting environmental requirements. Quality pulp can be produced using either a batch or continuous digesters.

3.2.4.1 Batch Digesters

Batch digesters are 170 to 225m^3 in capacity and are commonly fabricated from carbon steel with stainless steel liner that is used for pre-hydrolysis-type cooks. Screened chips are charged into the top of the digester. The volume of white liquor and black liquor required for the target active alkali percentage and liquor to wood ratio, respectively, is then metered simultaneously into the digester.

When the digester is fully charged with chips and liquor, it is capped. The batch digester is provided with a circulation system and heat exchanger for bringing the contents to pulping temperature. Direct heating by injection of steam with convection mixing provides goo results and forced circulation avoids liquor dilution, thereby maintaining higher alkali concentration during the cook and eliminating an additional load on evaporators.

A common circulation design draws liquor from a perforated ring near the mid-point of the digester through a heat exchanger, and distributes the return flow to both the bottom and top of the vessel. The circulating pump is usually sized to turn over the liquid contents of the digester about once every 10 minutes.

The loaded digester is brought up to maximum temperature according to a preset rate, usually controlled by a clock-driven cam.

3.2.4.2 Continuous Digester

In Continuous digester, the wood chips are fed from a surge bin through a volumetric chip meter and a rotary low pressure feeder into the steaming vessel. A slowly turning screw carries the chips though the horizontal steaming vessel, where flash steam at 1.05 kg/m^3 preheats the chips and drives off air and non-condensable. The chips then fall into a chute connected to the high-pressure feeder. The feeder consists of a single rotating element, when a filled pocket has moved 90°C, the chips are sluiced away with cooking liquor and carried up to the digester inlet.

Here, the slurry enters a cylindrical separator, perforations in the plate allow liquor to flow to the surrounding collection ring and be returned to the feeder, while the chips are pushed downward by a rotating helical screw. When the chips enter the digester, they have absorbed sufficient alkali to enable the chips to move downward by gravity through the liquor-filled space at the top of the vessel, until they settle on the chip mass.

The chips then moves downward as a uniform column without channelling (i.e. plug flow) through the digester zones where chips are impregnated with liquor through external heat exchangers. The retention time within the final zone is 45 minutes at 105 – 130°C.

The pulp is continuously slushed from the column of cooled, softened chips by slowly rotating paddles that are mounted on radical arms attached to the hub of the outlet device. The pulp is then blown at a precise rate of 200 psig to an atmospheric tank.

3.2.5 Processing of pulp

Pulps are subjected to a wide range of processing steps, depending on their method of preparation.

3.2.5.1 Deknotting

Knots are defined as the fraction of pulp that is retained as wood chips on a 3/8 perforated plate. These rejects may be true knots or uncooked chips. The knots are usually removed prior to pulp washing, either discarded as waste or returned to the digester in-feed. Pressure screen knotters are most commonly used. They consist of a totally enclosed cylindrical, perforated screen through which accepted stock flows. A rotating foil produces a series of pressure and vacuum pulses to keep the perforation clean. Knots are retained on the entrance side of the screen and are continuously discharged, along with some good fibre. The main drawback of the pressure knotter is the consequent need for a secondary screen to return good fibre back to the system.

3.2.5.2 Pulp washers

The cooked pulp from the digesters must be washed with the objective to:

- Remove residual liquor that would contaminate the pulp during subsequent processing steps; and

- Recover the maximum amount of spent cooking chemicals with minimum dilution.

There are a number of pulp washers that the industry uses i.e. rotary vacuum washers, diffusion washer, rotary pressure washer, horizontal belt filter, wash press and dilution/extraction. These methods are dependent on the fibre characteristics, shower characteristics, sheet formation and thickness and operating factors.

Rotary vacuum washers are the most used pulp washers and they consist of wire or clothed covered cylinder that rotates in a vat containing the pulp slurry. By means of internal valving and a sealed barometric down-comer, vacuum is applied as the rotating drum enters the stock. A thick layer of pulp builds up and adheres to the wire face as it emerges from the vat. Wash water is applied to displace the black liquor in the sheet as the drum continues to rotate. Finally, the vacuum is cut off and the washed pulp is removed from the mold. About 3 or 4 stages of washers are required to attain an overall satisfactory removal of about 99% of the washable liquor solids.

3.2.5.3 Screening

Screening is required to remove oversized, troublesome and unwanted particles from good papermaking fibres. Screens depend on the perforated barrier to pass acceptable fibre and reject the unwanted material. In most instances, it is the size of the perforations that determine the minimum size of debris that will be removed.

3.2.5.4 Centrifugal cleaning

Centrifugal cleaning removes unwanted particles (such as sand and dirt solids) from pulp by a combination of centrifugal force and fluid shear. Therefore, it separates not only on the basis of weight difference, but also particle shape to some extent. Centrifugal cleaners work on the principle of a free vortex generated by a pressure drop to develop centrifugal action. The stock enters the cleaner tangentially, the inlet scroll guides the flow to impact a rotating motion.

3.2.5.5 Thickening

Following low-consistency operations such as cleaning and screening, it is necessary to thicken the stock (with or without washing) prior to the next process operation. A variety of equipment is used for this operation and it depends mostly on the consistency of the final pulp that is required. Gravity thickeners are the most commonly used equipment. Water flows into the cylinder by virtue of the difference in liquid level between the vat and cylinder. Pulp is retained on the rotating cylinder and is couched off by a rubber roll.

3.2.5.6 Pulp storage

After thickening of the pulp into consistency of around 16%, it is stored for further use in the process. Pulp storage takes place at various points in the process to provide surge capacity and allow for interruptions in either supply or demand.

The final pulp storage takes place after pulp thickening. At this stage of the process, the pulp is ready to be sent to the paper machine for papermaking.

3.2.6 Recovery of Pulping liquors

The recovery of spent cooking liquors, the reconstitution of these liquors to form fresh cooking liquor, the realization of energy from incineration of organic residuals, and minimisation of air and water pollution, are all vital parts of the pulping process. These objectives are achieved through a well-defined series of steps, starting with the weak black liquor from the brown stock washers:-

- Concentration of liquor in multiple-effect evaporators to form strong black liquor;
- Black liquor oxidation;
- Further concentration of liquor to form heavy black liquor;
- Addition of salt cake to make up soda loss;
- Incineration of liquor in recovery furnace;
- Dissolving smelt from the furnace to form green liquor;
- Causticizing of green liquor with lime to form white liquor; and

- Burning of lime mud to recover lime.

By-product recovery

Two by-product of alkaline pulping are economically important i.e. turpentine and tall oil. Both products are obtained in quantity when pulping resinous woods such as pine.

3.2.6.1 Turpentine

Turpentine is recovered primarily from the digester relief gases. The gases are conducted to a cyclone separator where liquor carryover is removed, then to a condenser while giving up their heat to process water. The condensate drains to a decanter where the turpentine and water separate and overflow from top and bottom, respectively. The water is combined with other contaminated condensate streams for steam stripping, while the turpentine flows to a storage tank. While the turpentine sits in storage, additional water separates and settles to the bottom of the tank.

Chemically, turpentine consists of a number of cyclic compounds, principally pinenes and turpenes. The raw turpentine is sold to chemical processors where it is fractionally distilled and converted into numerous products, including camphor, synthetic resins, solvents, flotation agents and insecticides.

3.2.6.2 Tall Oil

The resinous material in pines and other species is made up fatty acids and resin acids, as well as sterols and related alcohols. During Kraft cooking, the fatty and resin acids become saponified (i.e. are made into sodium soaps).

During black liquor cooling and evaporation, the soaps and other precursors of tall oil become insoluble and rise to the surface of the liquor. The black liquor is usually concentrated to about 24% to 28% solids, then taken from one effect of the evaporators to a skimming tank where the soap is removed. The skimmed liquor is then returned to the next evaporator effect. The recovered soap is allowed to settle in storage to remove additional entrained liquor.

Some mills sell the recovered soaps to oil processing plants without further refinement. However, a large number of mills, especially where waste sulphuric acid is available from other operations, carry out an acidulation process to convert the soap into raw tall oil and recover the soda. The following reaction is typical:

$\mathrm{Na{\cdot}R} + H_2SO_4$ ------> $\mathrm{H{\cdot}R} + Na_2SO_4$

The acidulation mixture is either allowed to separate in a settling tank or is processed through a continuous centrifugal separator. The acid phase containing sodium sulphate and residual lignin is added to the black liquor system. The tall oil is washed with hot water to remove free acid and is allowed to settle in storage tanks prior to shipment.

3.2.7 Papermaking

Non-fibrous additive

A wide range of additives are added into a pulp stock to impart or enhance specific sheet properties or to serve other necessary purposes. These additives are classified as wet-end and dry-end chemistries. Wet-end additives are those additives that are added in pulp stock while the stock has a consistency of less than 3%. Below is the table depicting some of these additives and their application:-

Table 3.2 – Paper additives and their applications

Additive	Application
Sizing agents	Control penetration of liquids in the paper sheet
Wet strength resins	Add wet strength to such grades as towelling and wrapping
Fillers (e.g. clay, talc, TiO_2, etc.)	Improve optical and printing properties
Colouring materials (dyes and pigments)	Imparts desired colour
Retention aids	Improve retention of fines and fillers
Fibre deflocculants	Improve sheet formation
Defoamers	Improve drainage and sheet formation
Optical brightness	Improve apparent brightness
Pitch control	Prevent deposition and accumulation of pitch

Dry-end chemistries are added into the sheet of paper when the paper is dry to enhance the properties.

The basic component of the paper machine is stock inlet, head box, four-drinier wire, press section, dry section, calendar section and reel.

The **stock inlet** comprises of the screens and cleaners which acts as insurance against foreign contamination, although the pulp furnished to the paper machine should be reasonably free from impurities (assuming good screening and cleaning control in the pulp mill). These screens function mainly to remove gross contamination and to de-floc the fibres, while the centri-cleaners are designed to remove debris. The heart of the stock inlet is the fan pump which serves to mix the pulp stock and the water and deliver the blend to the head box. To ensure a uniform dispersion to the head box, the stock is fed from a constant head tank (called stiff box), through a control valve called basis weight valve, and is usually introduced axially into the suction line of the fan pump.

The function of the **head box** is to take the stock delivered by the fan pump and transform the pipeline flow into a uniform, rectangular flow equal in width to the paper machine and at uniform velocity in the machine direction. The following may also be listed as primary objective of the head box system:-

- Spread pulp stock evenly across the width of the machine;
- Level out cross-current and consistency variations;
- Level out machine direction velocity gradients;
- Create controlled turbulence to eliminate fibre flocking; and
- Discharge an even flow from the slice opening and impinge on the wire at the correct location and angle.

The **fourdrinier wire** is an endless, finely woven belt where the paper formation takes place. The sheet forming process involves water drainage, such effects as the generation and decay of turbulence, formation and breakdown of fibre networks, retention and transport of fine particles in the mat, compaction of the mat, and shear forces between the mat and free suspension. The most important effect of the drainage process is the dewatering of the fibre suspension to form the mat. When fibres are free to move independently of one another, drainage proceeds by the mechanism of filtration and the fibres are deposited in discrete layer. Filtration is the dominant mechanism in most fourdrinier forming applications. When the fibres in suspension are immobilized, they floc together in coherent networks, drainage then occurs by thickening and a more felted and floccy sheet structure results.

Papermaking suspensions spontaneously form networks during drainage, unless either sufficient dilution is used or supplemental mixing energy. Dilution is a powerful mechanism for dispersion, but the level required to adequately control flocking on paper machines is not economically feasible. Additional dispersion must be generated during drainage by the turbulence-inducing effects of drainage elements below the forming wire or by shear-inducing devices above the wire.

Once the paper sheet has been formed at the fourdrinier wire, it is then transferred into a **press section**. The primary objectives of pressing section are to remove excess water and to consolidate the sheet web. The press section also provides surface smoothness, reduce bulk and promote higher wet web strength for good runnability in the dryer section. The paper web is conveyed from the forming unit on a series of felts through the various presses and into the dryer section. The pressing section is considered an extension of the water-removal process that was started on the wire. It is by far more economical to remove water by mechanical means than by evaporation, so the papermaker is always looking for methods to improve pressing efficiency, reduce evaporation as well as reduce the evaporate load into the dryer section.

Sheet consolidation is a crucial phase of the papermaking process. It is here that the fibres are forced into intimate contact so that good fibre-to-fibre bonding develops during drying.

The objective of the **dryer section** is to evaporate the residual moisture in the pressed sheet at an efficient rate and at low steam usage. The wet paper from the press section containing about 60% moisture (40% dryness) is passed over a series of steam-heated rolls (usually of 60 or 72 inches diameter), where the moisture is evaporated and carried away by ventilation air. The wet web is held tightly against the rolls by a synthetic, permeable fabric called dryer felt. The dryer section is by far the most expensive part of the paper machine with respect to both capital costs and operating cost.

Machine **calendering** is the passage of paper through one or more nips formed by a set of iron rolls, and is the principal operation that is always carried out on machine. The sheet from a dryer section is passed through a machine calendering to reduce sheet thickness to the desired level, even out calliper variations so that a good reel can be built and impact desirable surface properties, primarily smoothness.

After drying and calendering, the paper must be collected in a convenient form for further processing in a **reeling section**. The reel drum called a pope reel is motor-driven under sufficient load to ensure adequate tension on the sheet from the calendars. During the normal operation, the web wraps around the drum and feeds into the nip formed between the drum and the reel held by the secondary arms. Paper builds up on the reel while an empty spool is positioned on the primary arms. Before the reel has built up to the required diameter; the new spool is accelerated up to machine speed by a rubber wheel and then loaded by the primary arms against the reel drum. When the reel's built-up is complete, the secondary arms release their pressure against the drum, causing the paper reel to slow down, a loop of paper then billows out between reel and drum, which is blown upward by air jets. At the proper moment, the back tender breaks the sheet at the loop so that it wraps the new spool. The full paper reel is then removed from the reel rails by a crane.

Once paper is established on the new spool, the primary arms are lowered so that the spool rests on the reel rails. The secondary arms then engage the reel spool to maintain the driving pressure of the reel on the drum. The primary are disengaged and returned to the upright position to receive a new spool.

3.3 Crude Tall Oil

3.3.1 What is Crude Tall Oil?

Crude Tall Oil (CTO) is a viscous yellow-black odorous liquid obtained as a byproduct of the Kraft process of wood pulp manufacture (Smook, 1997). Crude tall oil production process is depicted by a simplified diagram in Figure 3.2a and a detailed diagram in Figure 3.2b respectively. Crude tall oil is a major chemical by-product of the Kraft pulp industry. Its name comes from the Swedish word for pine, "tall", and indicates that the primary source is pine.

3.3.1.1 Origin of Crude Tall Oil

The resinous material in pines and other species is made up fatty acids and resin acids, as well as sterols and related alcohols. After the pulping process, the pulp is blown into the blow tank and the liquor is pumped to the evaporators to increase its solids to about 25%. This liquor contains tall oil soaps (sodium salts) and residual cooking additives i.e. sodium hydroxide and sodium sulphate. As the liquor leaves the digester to the evaporator, the concentration is about 15%, and the sodium salts (tall oil soaps) concentration is about 1.35 g/100g total solids. As will be discussed in the subsequent Chapters, the solubility of tall oil soaps depends on the total solids. At 25% and above, concentration of tall oil soaps, solubility drops. This can be attributed to the effect of ion that is caused by sodium (Na+) ions. At 25% and above, the high concentration of lignates causes tall oil soap to be soluble, and the rate of separation of soap on liquor that is skimmed off is slowed down by the apparent increase in viscosity. McSweeney (1987) cited this reduction in separation as the reason that the tall oil soap needs to be skimmed off when the liquor is at 25% solids and above.

The solids on the liquor are increased to 25% through evaporation, and the liquor is pumped into a skimming tank. These skimming tanks are normally arranged and operated in series. The liquor is pumped to the first skimming tank, where soap overflow on top and transferred to the second skimming tank. The underflow is concentrated further at evaporators to a concentration of 45%.

At the second skimming tank, the underflow is recycled at the recovery boilers. There is about 0.58g/100g of tall oil in this underflow which goes to the recovery boilers. A temperature of between 60°C to 100°C needs to be maintained as any drop in temperature will results in pumping problems for tall oil soaps (Gullichsen and Lindeberg, 1999)

Spent sulphuric acid is used to wash the crude tall oil soap before it enters the first storage tank. The soap is then pumped into the second storage tank until there is sufficient tall oil soap for the reaction. Depending on the size of the pulp Mill and the volume of the soap from the pulping process, a reaction is carried out once a day.

A pre-determined amount of soap is pumped into a reaction vessel that is usually made up of monel or nickel steel. Steam is injected into a reactor to heat up the mixture to a boiling point, and thereafter the acid is added. The optimum temperature for the reaction is achieved by the heat of dilution of the sulphuric acid. It is imperative at this stage to ensure that there is uniformity in the reaction, steam is therefore added at a pre-determined rate and constantly agitated by the use of mixers and stirrers. The reaction takes place for 2 hours and the pH is closely monitored. Once the pH reaches 4.0, the reaction is left to settle overnight. The corrosiveness nature of the sulphuric acid means that all metal pipes in the machinery used for the process must be constructed of stainless steel.

Below are the reactions that take place:-

Crude Tall oil

$$\text{R—COO}^{-}\text{Na}^{+} + \text{H}^{+} \rightarrow \text{R—COOH} + \text{Na}^{+}$$

This above reaction represents the ionic soap that is first converted into a carboxylic acid and then into an oil. This reaction is observed for both fatty acids and resin acids.

Lignins

$$\text{Lignite}^{-}\ \text{Na}^{+} + \text{H}^{+} \rightarrow \text{Na}^{+} + \text{lignin}^{2}$$

The above reaction explains the presence of sodium lignates that are precipitated by the acidulation reaction. An emulsion is formed between the oil phase and aqueous phase when settling takes place.

Calcium ions

The sulphate ions that are given off by the acid combine with calcium ions in the soap and they form a precipitate. Due to the weight/density of the precipitate, it settles at the bottom of the tank and follows the following reaction.

$$Ca^{++} + SO_4 \text{-------}\rightarrow CaSO_4(s)$$

Sulphide ions

Below are the important reactions that take place during acidification of the tall oil. There are substantial sulphide ions that are present during the tall oil soap reaction. When sulphuric acid added, protonation that results in the formation of H_2S takes place, and this is demonstrated in the following:-

$$S_2^- + H^+ \text{-------}\rightarrow HS^-$$

$$HS^- + H^{+\text{---------}}> H_2S$$

Care must always be exercised during the reaction at the tall oil plant as H_2S fumes are always likely to surface. There are always unwanted particles (CTO, emulsion for the lignin and aqueous), and these are pumped out of the mixture. Depending on the requirement, the mixture is left overnight so that it can settle.

Below is the procedure that is followed to treat the phases:-

- Hot storage is to store CTO prior to pumping it to other parts of the plants for further processing; and
- In order to extract the tall oil products from the crude tall oil, it is recycled and then pumped to the buffer tank. Hot water is pumped to the reaction kettle. Tall oil is then pumped into a centrifuge feed tank.

Calcium sulphate and lignin solids are removed and dumped at this stage of the process. This oil is not sufficiently pure and therefore cannot be pumped into the CTO storage tank. It is pumped back into the reactors and mixed with other soap batches.

Another phase of this process is aqueous phase. It is used in the initial part of the process which is to wash off acid before soap goes into the first storage tank. This phase is eventually sent to recovery boilers as a fuel source.

3.3.1.2 Yield during pulping

The normal yield is about 15-20 kg of tall oil per tonne of air-dried pulp, but for slow growing species of trees, up to 100 kg can be obtained. The average yield of CTO is in the range of 30-50 kg/t of pulp, which corresponds to 50-70% of the initial amount in the raw material used for pulping (Smook, 1992). This CTO is a saleable product for a pulping mill, but represents only about 1-1.5% of the mill's total revenue (Gullichsen and Lindeberg, 1999).

With the closing of the circulations in Kraft pulp mills, the role of the CTO plant has become more important, as it is a major source of sulphur for addition to the process and a part of the mill's waste handling and removal system. The availability of tall oil for a mill is greatly dependent on the wood species used for pulping, the growth conditions of the trees and the method and duration of storage of the logs and chips. Even among extractives-rich pine species, however, there is significant variation in the availability of tall oil (Gullichsen and Lindeberg, 1999; McSweeney, 1987).

3.3.1.3 Refining CTO

About 2 million tons of CTO are refined globally per year (Lindeberg and Ulmgren, 1996; Gullichsen and Lindeberg, 1999). There is little use for it in its raw state today, but it is purified and fractioned by vacuum distillation to yield following base products:

- tall oil fatty acids (TOFA);
- tall oil rosin (TOR);

- distilled tall oil (DTO);
- tall oil heads; and
- tall oil pitch.

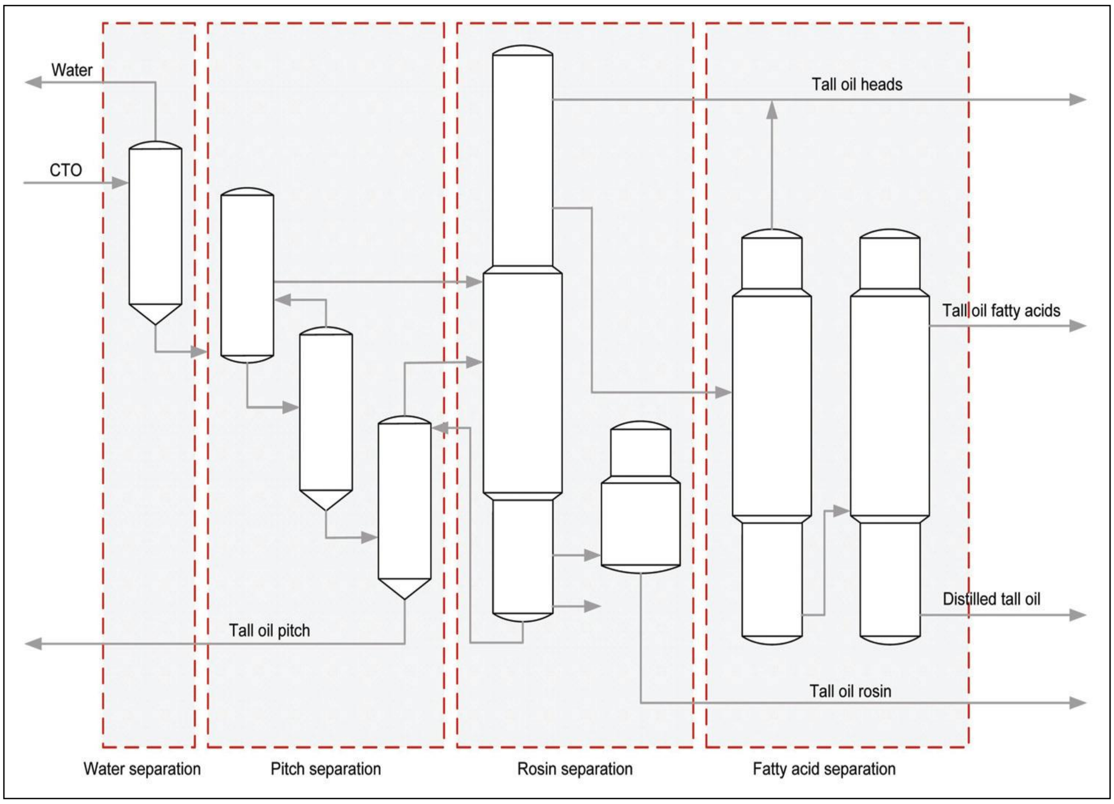


Figure 3.4 - Simplified diagram of the tall oil distillation process (modified from Anon. 2006, McSweeney *et al.* 1987, McSweeney 1989)

3.3.1.4 Uses of CTO

Tall oil products have a wide range of applications, and the various base products can be further refined into a wide variety of products and formulations. **Tall oil fatty acids** are used as raw materials for the manufacture paint vehicles, soaps/detergents, printing inks, foam inhibition agents, lubricants, greases, flotation agents and industrial oils. **Tall oil rosin** has traditionally been used as a paper size, but this use is declining. Other applications include alkyd resins, printing inks, adhesives, emulsifiers, paint and lacquer vehicles and soaps. **Tall oil pitch** has some special applications as an asphalt additive and in rust protection, printing inks and oil-well drilling muds, but its primary use is still as a sulphur-free fuel. (Grace, 2001; Gullichsen and Lindeberg, 1999).

CTO can also be used as a lime kiln fuel, which is an attractive alternative when it is of poor quality. It can replace the primary fuel oil partially or totally and has almost the same heat value and combustion properties (Gullichsen and Lindeberg, 1999). Emission trading has further increased the attractiveness of this alternative nowadays.

3.3.1.5 Chemical composition and characterization of crude tall oil

The dark-coloured crude tall oil (CTO) is not composed of pure triglycerides like other vegetable oils, but is rather a mixture of fatty acids, rosin acids and unsaponifiable substances, e.g. sterols, waxes and hydrocarbons. The precursors of CTO are the extractives found especially in coniferous trees. Pine typically contains extractives such as free resin acids, fatty acids in the form of glycerides, and turpenes. The extractives also contain neutrals or unsaponifiable that are primarily alcohols of various kinds.

Several carboxylic acids, fatty acids and rosin acids are found in crude tall oil. The predominant fatty acids, contributing the bulk of the observed physical and chemical properties, are oleic and linoleic acids (Duncan, 2003), whereas the main resin acids are abietic-type acids and primaric-type acids (Haas, 2005).

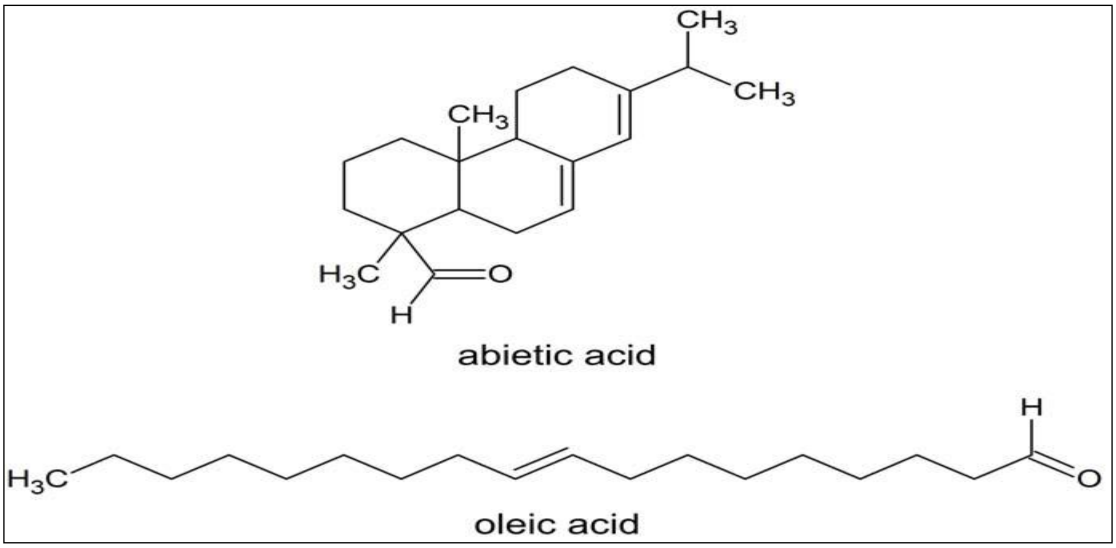


Figure 3.5 - The structure of resin (abietic) and fatty (oleic) acids prominent in crude tall oil

The figure above represents the structure of resin and free fatty acids in the Crude Tall Oil. It can be observed that abietic acids molecules are multi-ring and bulkier compared to oleic molecules which are straight chained molecules.

CTO varies considerably in composition and quality depending on the location of the mill, time of year, growing cycle of the tree, tree species, ageing of the wood, amount of heartwood, pulping conditions, handling and storage of the wood and the efficiency of the system used to recover the tall oil (Anon, 2006: Gullichsen and Lindeberg 1999). Furthermore, storage of CTO leads to esterification of the sterols and other alcohols with fatty acids (Holbrom, 1978, Avela and Holbrom, 1971a; Avela and Holbrom, 1971b), which will reduces the number of acids it contains and increase its hydrophobicity.

3.3.1.6 Analyses of CTO

A commonly used measure of tall oil quality is the acid number (AN), which indicates the number of carboxylic acid groups (total fatty and resin acid content). Mills that use only pine have the highest quality CTO, with AN values of 160-165 mg KOH/g oil, whereas mills that use 50% or more hardwood in their furnish have a CTO with an Acid Number of 125-135 (Kusdiana and Saka, 2001).

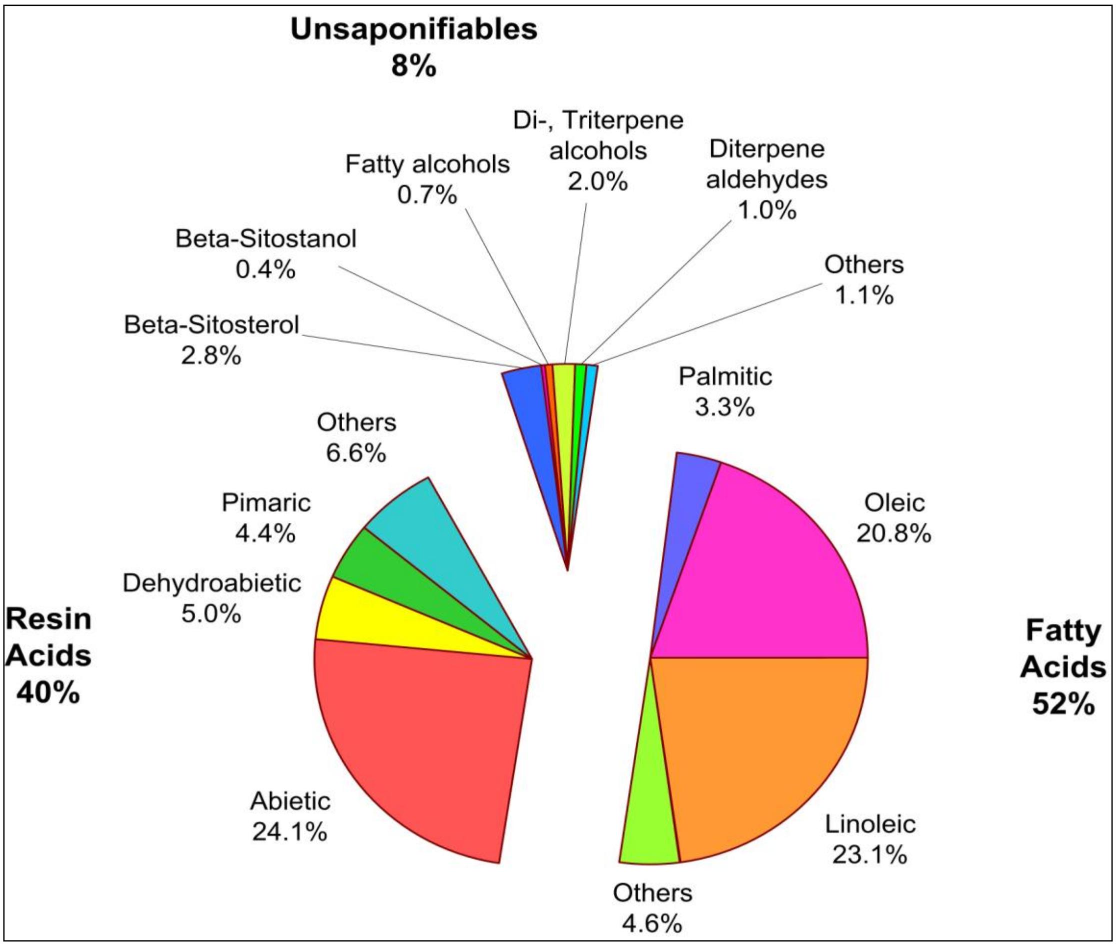


Figure 3.6 – Typical composition of crude tall oil, w/w (Southern US)
Source: Schulte, W.S. 2007:11

Biodiesel production could be a very important use for the fatty acids found in CTO. The fuel properties of biodiesel containing resin esters would require further investigation, particularly when blended with petro-diesel or with biodiesel fuels derived from different feedstocks.

3.4 Biodiesel

3.4.1 Introduction

Biodiesel is defined as the alternative fuel that is produced from vegetable, animal and spent oils (Kusdiana and Saka, 2004). Biodiesel can be used as a substitute for the diesel fuel or can be used a blend. With the exception of the Cetane number that is higher, other characteristics and parameters are similar with the diesel fuel for the biodiesel which enables its use to diesel engines without any significant modification to the engine. There are also other downstream benefits of using the biodiesel which are related to the greenhouse effect and will be explained later in this report

Since biodiesel is biodegradable, and it does not contain sulphur and other aromatic components, it offers the benefit of potentially reducing the particulate and other emissions that are toxic. Jerry (2007) reported that adding small amounts of biodiesel to conventional diesel can improve fuel lubricity, extend engine life, and increase fuel efficiency.

3.4.2 Background

Rudolph Diesel inverted the diesel engine in 1900 (Nitske, 1965). He converted vegetable oils into biodiesel for the first time. There were further research studies that followed which were focused on alternate raw materials and improving the quality of the biodiesel. Though most of the research was carried out of interest, the shortage of fossil fuels prompted the countries around the world to consider seriously the need for alternate fossil fuels (Knothe, 2001).

The political intervention and the declaration of peace after the 2nd world war, eliminated the shortage of fossil fuels and the need for the research on biodiesel was reduced (Johnson, 2006).

Petersen and Gregory (2005) cited the following reasons to the increase in interest in biodiesel production:

- formation of OPEC around 1970’s;
- increase in prices for fuel; and
- possibility of fuel shortage.

There were also incentives that were introduced around 1991 that prompted the need for biodiesel.

3.4.3 Biodiesel Use

There are a number of biodiesel uses that have been studied in the literature, and have been successful tested and implemented in the engines. They utilise biodiesel as a blend with other diesel product or in its pure state depending on the required engine performance.

Pure state

This is the ideal state or form to use biodiesel as most of the documented advantages of biodiesel are realised e.g. reduction in carbon monoxide excretion, unburned hydrocarbons, etc. However, Biodiesel education (2006) listed the following disadvantages that are associated with using biodiesel:

- possibility of deposits in fuel tanks resulting from unburned hydrocarbons;
- degrading of fuel lines because of incompatibility of biodiesel and the material of construction; and
- paint damage along fuel fill ports.

Blend state

Friedrick (2003) said biodiesel is also used as a blend with fossil diesel to eliminate the highlighted problems in the paragraph above, while benefiting from advantages of biodiesel. This blend can blend up to 50% (biodiesel/fossil diesel) and is normally expressed in terms of the biodiesel content in the blend e.g. B50 (indicating that there is 50% biodiesel in the blend).

Additive

Friedrick (2003) said biodiesel can also be used as an additive during lubrication. There has not been much research work conducted on this aspect, but the cost-effectiveness that is provided by biodiesel as a lubricant enhancer makes it an interesting research area that requires further exploring.

3.4.4 Advantages of biodiesel use

Using biodiesel has the following advantages for consumers (Journey to Forever, 1999):

- There is no specific need for modifying the diesel engine, if switching to biodiesel;
- Biodiesel burns 75% cleaner than diesel is considered environmentally friendly;
- Biodiesel is unlikely to contribute to the depletion of the ozone layer because there is no net carbon dioxide that is emitted in the exhaust fumes;
- Biodiesel is biodegradable and is also not toxic; and
- Biodiesel offers the extension of a life of an engine due to its lubricant characteristics and the cetane number that is higher that diesel.

3.4.5 Disadvantages of biodiesel use

Beer and Grant (2005) listed the following as the disadvantages of using biodiesel:-

- Biodiesel produces high levels of NO_2 because of the high oxygen content. This happens mostly during combustion, and can be neutralised by the use of a catalytic convertor and adjusting the timing of the engine;
- Care needs to be exercised during storage of biodiesel because it has a low oxidation stability level. Also, because biodiesel is hygroscopic in its nature, and contact with humid air should be prevented;
- In certain cars, because biodiesel has a lower volumetric density compared to fossil fuel, it is possible that for a similar distance covered the usage might be higher;
- Biodiesel has a higher cold-filter plugging point temperature than fossil diesel which means it will crystallize into a gel at low temperature when used in its pure form;
- It can cause dilution of engine lubricant oil, requiring more frequent oil changes than in standard diesel-fuelled engines;

- Biodiesel is a strong solvent and scrubs out all the tars, varnishes, and gums left by fossil diesel in the fuel system which means that the fuel filter will have to be replaced a few times during the initial stages of biodiesel use; and
- A modified refuelling infrastructure is needed to handle biodiesel, which adds to their total cost.

3.5 Generic oil conversion procedures into biodiesel

There are a number of generic conversion procedures that have been traditionally used to convert oil into biodiesel. These procedures have utilised vegetable oils because they offer good ignition characteristics and have been used as fuels in diesel engines in times of fuel shortages (Friedrick, 2003). However, some of the properties of vegetable oils, especially their viscosity and quick oxidation tendency, make them undesirable for use in modern diesel engines.

The viscosity of vegetable oils, when used as fuel, can be reduced in at least four different ways:

- Dilution;
- Pyrolysis;
- micro emulsion; and
- Trans-esterification.

Of the above options, transesterification is the current method of choice, by which vegetable oils can be converted into the products known as "Biodiesel", with properties very similar to diesel fuel. Biodiesel can be used in its neat form or as a blend in conventional diesel fuel. Various types of animal fats, used oils and fats, and micro-algal oils can also be converted to biodiesel type products. Two technologies exist for the conversion of vegetable or biomass derived oils and animal fats to biodiesel.

3.5.1 Biodiesel by Esterification Process

The conversion procedure that has been used over the years to convert vegetable oils and other forms of oils/fats into biodiesel in the presence of an catalyst is called Esterification Process (Biodiesel Education, 2006). This process involves combining oil (main raw material) with an alcohol base (either ethanol or methanol) depending on their availability and costs as well as the final product required. The process also used a carefully selected catalyst (Na + KoH) to form methyl ester. The above process offered the following advantages:

- reduction of 1/3 of the molecular weight to that of the oil;
- reduction of the viscosity by 1/8; and
- an increase in the volatility.

The following are also process variables that need to be taken into cognisance during transesterification as they affect the reaction time and the efficiency of the process i.e.

- Process temperature;
- Type and the concentration of the catalyst used;
- Feedstock to alcohol ratio; and
- Mixing time.

Also, the extent to which the reactants are pure (e.g. any presence of contaminants since the raw materials are by-products) is also crucial for the successful conversion.

A stoichiometric material balance yields the following simplified equation:

Oil or Fat (1000kg) + Methanol (107.5 kg) = Methyl ester (1004.5 kg) + Glycerol (103 kg)

After the reaction, the products are separated into two phases which facilitates easy removal of glycerol, a valuable industrial by-product, in the first phase. The remaining alcohol/ester mixture is then separated and the excess alcohol is recycled. The esters are sent to the clean up or purification process, which consists of water washing, distillation, vacuum drying, and filtration. The biodiesel produced from this process is commonly referred to as "vegetable ester".

3.5.2 Biodiesel by Hydrogenation Process

The second process, which involves simultaneous catalytic hydrogenation and cracking of vegetable and tree oils, was developed at the Saskatchewan Research Council under the sponsorship of the (CANMET) Canada Centre for Mineral and Energy Technology (Johnson, 2006). This process has been used to produce biodiesel type material from "Tall Oil", a by-product from the Kraft pulping process. The principal constituents of tall oil are the unsaturated C18 fatty acids, resin acids and unsaponifiable hydrocarbons such as di-terpenic alcohols/aldehydes. The biodiesel produced from this process has been given the name "SuperCetane", due to its high cetane number which is close to 60 (Canacki and Gerpen, 2001).

CANMET technology has been licensed to Arbokem of Vancouver, Canada, to market the process worldwide. The world production of tall oil is estimated to be a potential 1.2 million tonnes/year. Well over 60% of that comes from the U.S. BC Chemicals is a leading producer of tall oil in Canada (Canada Times, 2007).

In its traditional use, the crude tall oil (CTO) is first de-pitched and then upgraded by distillation to produce more valuable products such as tall oil fatty acids (TOFA) and tall oil rosin (TOR). The CANMET process which is known to convert tall oil into higher value products, involves simultaneous catalytic hydrogenation and cracking of the de-pitched tall oil (DPTO). Two continuous trickle bed reactor systems were used in this programme. The first unit, a once through semi-pilot plant with a 750 ml reactor was used for the initial work. The second system uses a process development unit (PDU) with a 10 litre reactor which fully simulates the features of the process in commercial units, and was used to produce sufficient quantities of SuperCetane for engine testing.

In the production process of SuperCetane, the DPTO feed is pumped into the high pressure system where it combines with hydrogen. This gas-liquid phase passes through a series of electric pre-heaters before entering the catalytic trickle bed reactor. The product is collected in two flash columns, decanted to remove the water and then distilled in a batch unit to obtain the desired cut.

The process gas is recycled after removing the impurities in a series of scrubbers. Long duration pilot-plant runs were successfully carried out at CANMET's Energy Research Laboratories in Ottawa, to convert tall oil into SuperCetane, and the process is now ready for scale-up to industrial levels.

The production costs for SuperCetane including the capital and operating costs in a large scale plant is estimated at 10 to 12 cents per litre (Mittelbach and Remschmidt, 2005). The cost of the tall oil as raw material could vary from 8 to 20 cents per litre of SuperCetane. The total cost of this biodiesel product could range between 18 to 32 cents per litre, which makes it economically more attractive than vegetable esters currently costing about 66 cents per litre.

3.5.2.1 Attempts to reduce cost of biodiesel

Between 75 and 90 per cent of the cost of biodiesel is the raw material (Pramanik and Tripathi, 2005). In order to reduce the cost of biodiesel, it is imperative to find oils sources that have less competition, and where biodiesel could reign as the primary consumer. One possibility is waste frying oils. In selecting a feedstock, the cost of raw materials, as well as the processing cost and its effect on the quality of biodiesel and other by-products, need careful assessment.

3.6 Crude tall oil and tall oil fatty acids conversion procedures

A number of procedures have been researched by different authors to convert oils with high free fatty acids content into biodiesel. Below are the common procedures that this report will discuss:

- Base-catalysed transestefication;
- Acid-catalysed esterification;
- Acid/base reactions;
- Enzyme catalysed reaction;
- Hydroprocessing; and
- Supercritical methanol treatment.

All of the above methods have been reported to show successes in the production of diesel-equivalent biofuels. There are however predefined conditions (e.g. purity and quality of the feedstock) for these procedures to be effective in conversion feedstocks into biodiesel.

3.6.1 Base-Catalysed Transesterification

The success stories and research studies for biodiesel has mostly been those that used vegetable oil as a raw material. Vegetable oils contain less free fatty acids (below 2%) which make the conversion into biodiesel a lot easier. Also, the availability of the base catalyst (NaOH or KOH) has also made base catalysed transesterification the most common used conversion procedure.

Also, base-catalysed transesterification has been sparingly used but there have been noted disadvantages with this procedure i.e. unfavourable and robust conditions as well as longer reaction time for complete reactions (Canacki and Van Gerpen, 2001).

Sodium hydroxide (NaOH) and potassium hydroxide (KOH) are common alkaline catalysts that are used during base esterification of triglycerides, but are however not effective in esterifying free fatty acids. The figure below demonstrates the transesterification process:

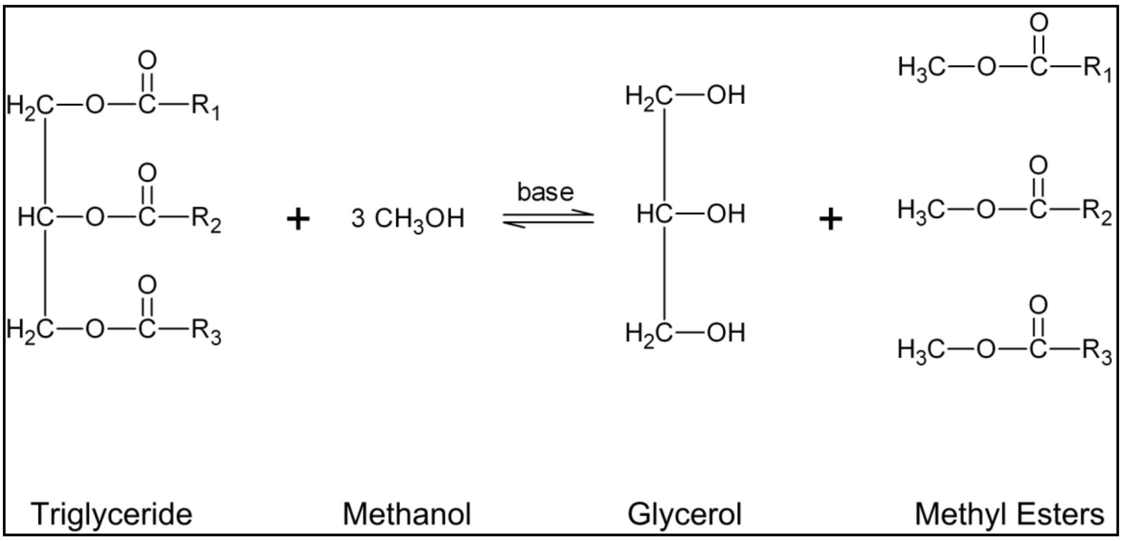


Figure 3.7 Base-catalysed transesterification reaction

From the above figure, it can be observed that transesterification takes place when an ester reacts with an alcohol to form a different ester. The chain of fatty acids that is connected to the glycerol backbone gets broken down at ester bond, and reacts with alcohol to form alkyl esters and glycerol molecules.

A number of authors have investigated the transesterification reaction process and have concluded that is influenced by a number of process variables, i.e. feedstock to alcohol ratio, type and concentration of catalyst used, reaction time and reaction temperature, and free fatty acids. Canacki and van Gerpen (2001) reviewed this process and discovered that when the free fatty acids content in the feedstock exceeds 2%, especially in crude material, it results in process problems and eventually affect the final biodiesel quality and output.

Aracial, Mercedes and Gemma (2005) also reviewed the transesterification process and found the following problems as indicated by the Figure 3.7 below:

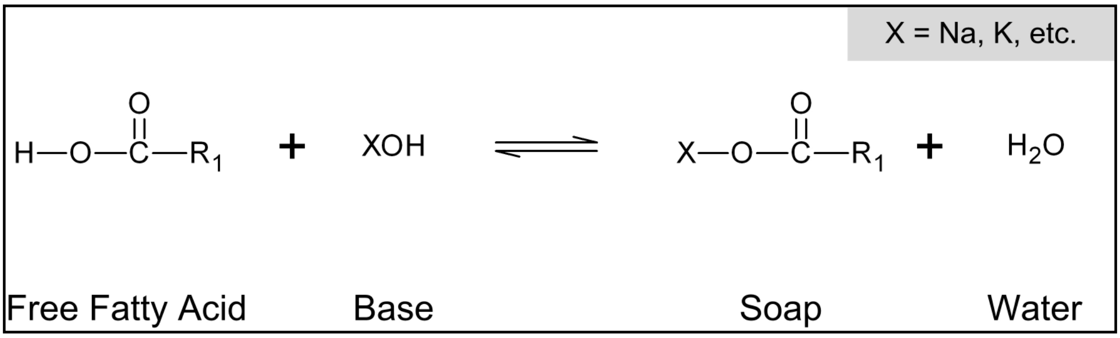


Figure 3.8 Undesired saponification reaction

They discovered that there were problems with the depletion of catalyst, formation of soap and difficulties related to saponification reaction.

Also, Mattingly (2005) used the base catalysed transesterification to convert chicken fat into biodiesel. He concluded that since chicken fat had higher free fatty acids, above 2%, transesterification process was not possible as similar problems that have been experienced by other researchers were observed with chicken fat. He also considered a sample of tall oil, and concluded that it would be impossible to convert tall oil using base catalysed transesterification as it contains high free fatty acids.

3.6.2 Acid-catalysed Esterification

This is also an effective conversion procedure that has been extensively used for feedstocks with free fatty acids that are above 2%. This procedure uses an acid catalyst (H_2SO_4). As stated before in this document, acid catalysts are unable to transesterify glycerides, but they are able to esterify free fatty acids. The figure below represents this acid-catalysed esterification process.

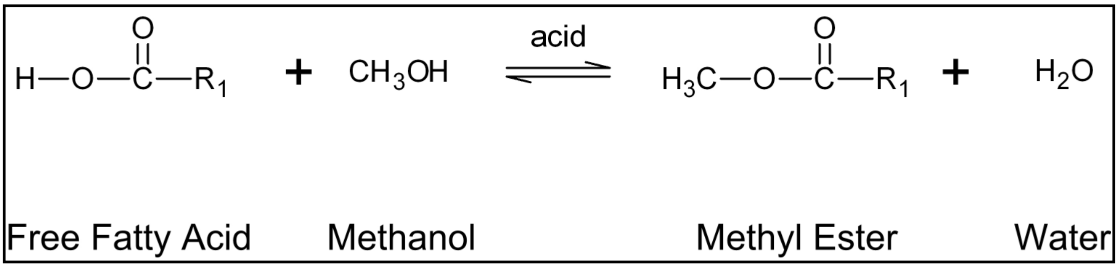


Figure 3.9 Acid-catalysed esterification reaction

The above figure represents the esterification process, where in the presence of acid catalyst, free fatty acids and methanol reacts to form alkyl esters and water.

Many authors and researchers have been able to esterify feedstocks containing high free fatty acids with much success. Jaayarajal *et al* (2005) were able to esterify free fatty acids that are found in rubber seed oil using a sulphuric acid catalyst. In their multiple step process study, they discovered that during esterification the acid content dropped from 17% to 2%. They also used an alkaline catalyst where triglycerides that were remaining in the oil were transesterified.

A distinct difference in definition needs to be drawn at this stage between acid-catalysed transesterification and an acid-catalysed esterification. The term transesterification is used to describe the reaction of an ester and alcohol to form a different ester and esterification is used to describe the reaction of an acid and alcohol to form an ester (Schulte, 2007).

A number of authors (Mattingly, 2005; Dalai, Ajay and Mangesh, 2006; Canakci and Van Gerpen, 2001) have also used a multistep process on the feedstock that had high free fatty acids and arrived at similar conclusions. They went a step further and recommended a kinetic rate expression for the esterification of free fatty acids in the presence of triglycerides. They also discovered that the reaction was quicker in a batch set-up where no product was removed and obtained yields of more than 79%.

Also, Haas (2005) adopted a different angle from the other previous researchers and the work is represented below:

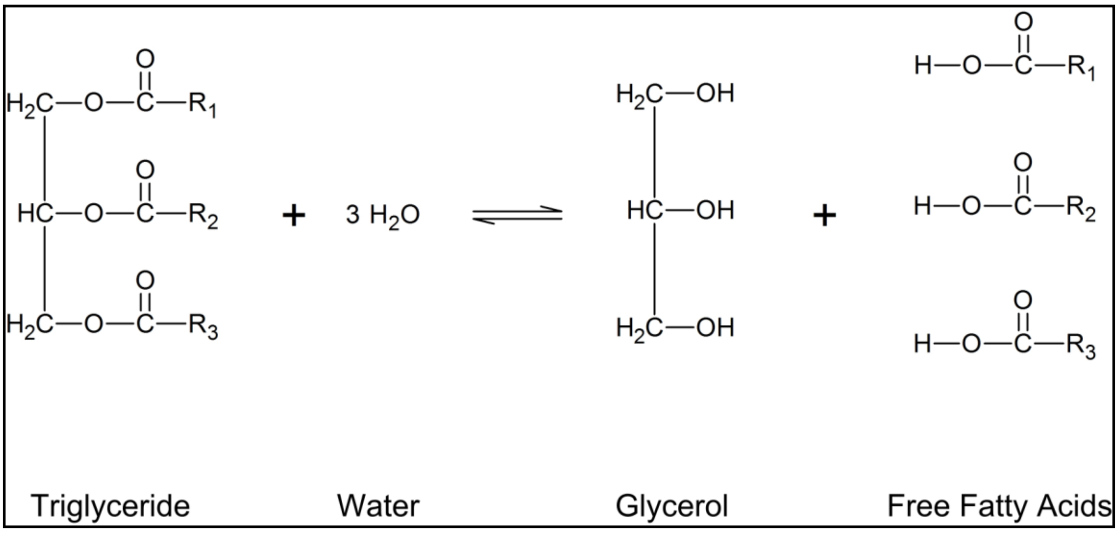


Figure 3.10 Hydrolysis of triglycerides

The above figure represents the research conducted by Haas (2005). In this study, the feedstock was the low quality soybean oil. The study began by hydrolysing all triglycerides in the feedstock. The hydrolysis process formed free fatty acids as well as glycerides. Glycerides were removed and the free fatty acids were esterified using an acid catalyst. In the conclusion, it was discovered that the additional processing of lower quality feedstock did not significantly increase the cost of biodiesel. Haas also performed an economic feasibility study on his research and concluded that it was still 25% cheaper to use the lower quality feedstock as raw material.

Also, as can be seen in Figure 3.9, it is a reverse reaction. The forward reaction is inhibited by water that is produced during the reaction. It is also for this reason that Di Serio et al (2005) discovered that their reaction during their study was limited above 80% yield. This indicates that on the final product, there will be about 20% of unreacted material.

Canakci and van Gerpen (1999) observed that even 0.1% of water present in the reactants has a potential to retard the production of methyl ester (biodiesel). They went further by determining that 5% additional water can reduce the conversion by at least 6%. This indicates that low tolerance that acid-catalysed reaction has on water. Canakci van Gerpen (2001) worked further on the procedure and discovered that an additional water removal step in the esterification reaction can significantly reduce the quantity of catalyst used, reaction time and alcohol that is used and thereby improve the efficiency of the process.

Normally, there is a ratio of 30:1 between an alcohol and a feedstock that is required to produce quality biodiesel. Any savings on the alcohol can significantly reduce the overall cost of biodiesel production.

Steinigeweg and Gmehling (2003) esterified free fatty acids feedstock by using a reactive distillation process. They succeeded in producing a cost effective biodiesel because they reduced the amount of alcohol and catalyst that was required while the process proceeded to completion. Their invention was to reduce water and esters continuously, though his procedure still made use of an acid catalyst.

From the above explanations, it would appear that acid catalysed procedure is appropriate to convert Crude Tall Oil and Tall Oil Fatty acids into biodiesel. But due to the high levels of triglycerides in our feedstocks, longer reaction time, the acid catalysed method is also inappropriate for this study.

3.6.3 Enzyme Catalysis

One method that has gained attention recently is the use of enzymes to catalyse the transesterification and esterification reactions. Under mild reaction conditions, specific enzymes can transesterify triglycerides and esterify free fatty acids in a single step process at their chemically active sites. Particular enzymes are carefully selected for their ability to perform these two reactions. Their use can prevent by-product formation (including soaps) and allow for simple product and catalyst recovery. Enzyme catalysis therefore has the potential to eliminate some of the problems associated with the acid- and base-catalysed methods. Furthermore, Gupta, Shweta and Shweta (2004) demonstrated that a lower alcohol to oil ratio is needed for enzyme catalysis and that high yields can be obtained. For the transesterification of Jatropha oil using the Chromo bacterium viscosum lipase, an ethanol to oil ratio as low as 4:1 resulted in a 92% conversion to ethyl esters at only 40 ºC.

Kobayashi *et al*., 2005 saw similar conversions of high free fatty acid oil using the Candida Antarctica lipase at 30 ºC in a multi-step process. While the use of enzymes has many advantages over traditional methods of biodiesel production, there are several reasons why their use is only seen on a laboratory scale. Some of these disadvantages include the high costs of the enzymes themselves, the long reaction times required for acceptable conversions, enzyme inactivation by certain contaminants, as well as water inhibition. In the conversion of Jatropha oil, Gupta *et al* (2004) required 15-25 hours for the reaction to reach >90% conversion, while Kobayashi *et al* (2005) required more than 50 hours using the Candida Antarctica lipase. In comparison, traditional base catalysed transesterification can be achieved in about one hour. These long reaction times inhibit most industrial applications. To an extent, these times can be shortened with additional enzyme use, but then catalyst material and processing costs are increased.

While more refined feedstocks can be used to prevent enzyme inactivation, the additional cost of the raw materials can become unacceptable. Furthermore, the conversion of free fatty acids, such as those in tall oil, will result in water formation that could inhibit the catalysts and complicate the reaction scheme. Gmehling and Sven (2003) reviewed many other studies on the use of enzymes for biodiesel production and reported many of these same advantages and disadvantages. These studies have led to the formulation of optimal reaction conditions that can be found in the aforementioned literature, and can depend on the particular enzyme used. While there is great promise for enzyme catalysed biodiesel production, due to the high costs of the enzymes, long reaction times required for high conversions, and enzyme sensitivity to contaminants, traditional chemical catalysts are more economical at this time.

3.6.4 Hydro-processing

All of the previously discussed biodiesel production methods have involved alkyl ester formation from the reaction of a short chain alcohol (i.e. methanol) with triglyceride or free fatty acid molecules. These methods have taken advantage of the carboxylic moiety present in the feedstock. The removal of this carboxyl group as well as any unsaturated bonds results in a mixture of hydrocarbons, mainly alkanes, which are also useful as a diesel-grade fuel. A multi-step process involving the catalytic hydrogenation of any unsaturated bonds and the thermal and/or catalytic cleavage of the carboxylic group (either by decarboxylation or hydrodeoxygenation) can achieve both of these objectives.

These processes are well understood in the petroleum industry, and are generalized in Figure 3.10 and Figure 3.11 (Dykstra et al, 1988). Thus, these hydroprocessing reactions were investigated for the conversion of bio-renewable feedstocks by Terry and Petri (2006).

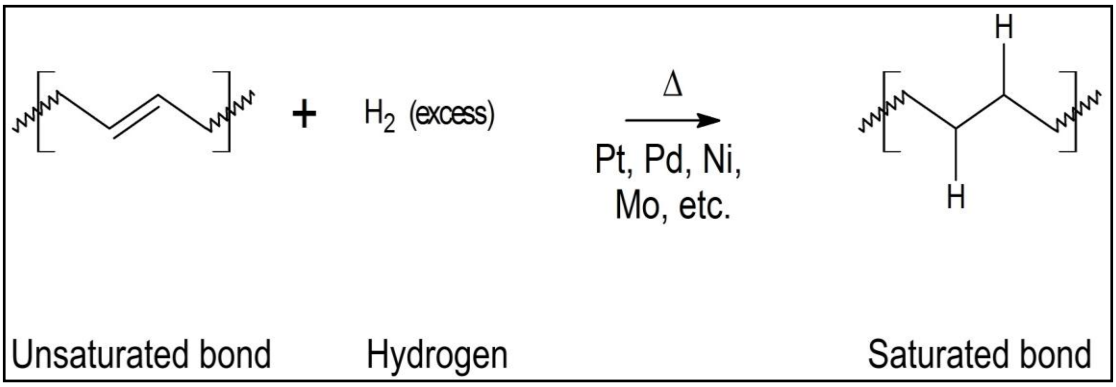


Figure 3.11 Catalytic hydrogenation of unsaturated bonds

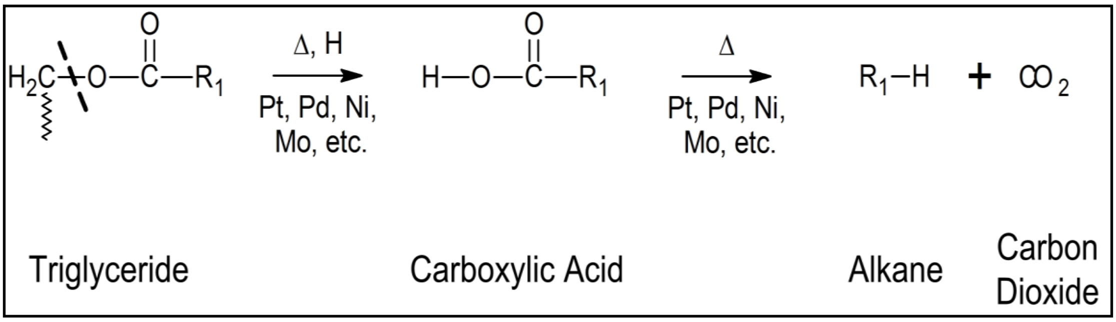


Figure 3.12 One reaction pathway for decarboxylation/hydrodeoxygenation of triglycerides

A patented process describes the hydrogenation and decarboxylation, (or hydrodeoxygenation) of soybean oil with hydrogen using a heterogeneous nickel or nickel/molybdenum catalyst at 300 - 350°C and 35 bar. The oil is fed into one or more catalyst beds in the presence of hydrogen. Under these conditions, the hydrogenation and decarboxylation/hydro decarboxylation reactions proceed, eliminating the carboxyl functionality and any unsaturated bonds. Some by-products, including water, light hydrocarbons, and some heavier hydrocarbons must be separated to obtain the final biodiesel product. Yields of diesel-substitute fuels of up to 98% were obtained from the refined soybean oil. Interestingly, crude tall oil was also tested under these conditions, giving a diesel-fuel yield of 76%, with a large portion of the by-products consisting of carbon dioxide and carbon monoxide. The importance of feedstock pre-treatment was noted, as some impurities could poison the catalyst. The patent also suggests the use of an isomerisation post-treatment to improve the cold-flow properties of the saturated alkanes, which would otherwise have a higher viscosity and cloud point (Jerry, 2007).

Hogan et al. (1996) describe the simultaneous catalytic hydrogenation and cracking of de-pitched tall oil to obtain diesel fuel additives. While no specific catalyst is mentioned in the work, the reactor system is similar to the process described above. Although Hogan et al. (1996) obtained diesel fuel yields of only 60%, other by-products such as the light and heavy-end hydrocarbons were also useful as fuels. Coll, William and Udas (2001) reported on similar hydro-treatment of the rosin acid fraction of tall oil using a variety of solid catalysts.

Diesel-grade fuel yields in excess of 80% were obtained, but the measured Cetane Number was found to be less than that of biodiesel from traditional methods.

As one of the refining techniques that are commonly used in the petroleum industry, because of their high suitability, the hydroprocessing reactions discussed above show promise for bio-fuel production. High yields have been observed for more refined vegetable oils, the technology is well proven, and the process can be readily installed at existing petroleum refining plants. Also, promising is how this method can treat feedstocks that contain both free fatty acids and triglycerides. However, coke formation and catalyst poisoning can cause problems for the solid catalyst(s), requiring regeneration or costly replacement. Though not reported, the degradation of triglycerides can also result in several other types of hydrocarbons such as alkenes, alkadienes, and some aromatics (Dykstra *et al*., 1998). The by-products of this method may even include undesirable greenhouse gases such as carbon dioxide and carbon monoxide. These by-products reduce the yield and efficiency of the process, as these must be removed from the final product through costly operations such as distillation, amine absorption, and/or pressure swing adsorption.

Also, the elimination of oxygen from the fuel may also reduce or eliminate the beneficial properties of biodiesel, such as the cetane number, lubricity or solvent capability as mentioned earlier. Finally, the need for a separate isomerisation step to improve cold-flow properties is also a disadvantage, resulting in further complexity.

3.6.5 Supercritical Methanol Treatment

A supercritical fluid is any substance at a temperature and pressure above its critical point (Bart, 2005). It can diffuse through solids like a gas and dissolve materials like a liquid. Supercritical methanol treatment dissolves and causes a reaction between components of a product – in this case, crude tall oil and tall oil fatty acids – by subjecting the product to high temperature and pressure. Substances become “supercritical” when they are heated and pressurized to a critical point, the highest temperature and pressure at which the substance can exist in equilibrium as a vapour and liquid. The simple, one-step process does not require a catalyst.

Du *et al*, 2006; Kusdiana, (2001) at ambient conditions, the non-polar compounds, i.e. free fatty acids and triglycerides are insoluble in methanol, which is a known polar compound. Also, during the reaction between free fatty acids/glycerides and methanol, the system becomes heterogeneous especially if no catalyst is used (either acid or alkaline), and, hence, separate layers that are not in solution are formed.

These two layers make it difficult for the reactants in a reaction to come into contact, and hence the long reaction time of about 10 hours (Diasakou et al., 1998).

The above highlights the importance of a catalyst in these esterification reaction processes. The catalyst also promotes the nucleophilic attack of methanol on the carboxyl groups in the feedstock, increasing the reaction rates of esterification or transesterification (Ataya, Marc and Marten, 2006). A similar mechanism is observed with heterogeneous catalyst, though the enzymatic catalyst follows a different approach because, instead of attacking carboxyl groups in the feedstock, it attacks selected and highly active sites in the feedstock to achieve the results of the reaction faster.

The procedures that have been discussed, i.e. base-catalysed esterification, acid-catalysed transesterification require that the feedstock, with high free fatty acids be pre-treated prior to converting into biodiesel. This pre-treatment adds to the overall costs of biodiesel production and makes the process uneconomical. Therefore, a biodiesel production procedure, that would be able to treat feedstock with high free fatty acids without prior pre-treatment, was investigated. This procedure would also ensure that there is sufficient contact between feedstock and alcohol during the reaction while, at the same time, not using catalyst. This process is called **Supercritical methanol treatment procedure**.

This procedure involves charging reactants into a batch reactor and operating the reactor at temperatures and pressures above the critical point of methanol (Tc = 240 °C, Pc = 35 bar). The effectiveness of supercritical methanol treatment procedure depends on the temperature and pressure effects on the thermo-physical methanol properties, such as viscosity, diffusivity, density and polar (Demirbas, 2006; Kusdiana and Saka, 2001).

When treated beyond its critical point, methanol no longer has a distinct liquid or vapour phase as can be seen in Figure 3.13 below, but rather a single fluid phase (Biodiesel Education, 2004). With this phase change, methanol possesses an increased mass diffusivity, decreased viscosity, and a density that can be manipulated over a large range through relatively small changes in temperature and pressure (Schulte, 2007). These fluid properties allow supercritical methanol to be used as a tunable solvent with superior mass transfer characteristics.

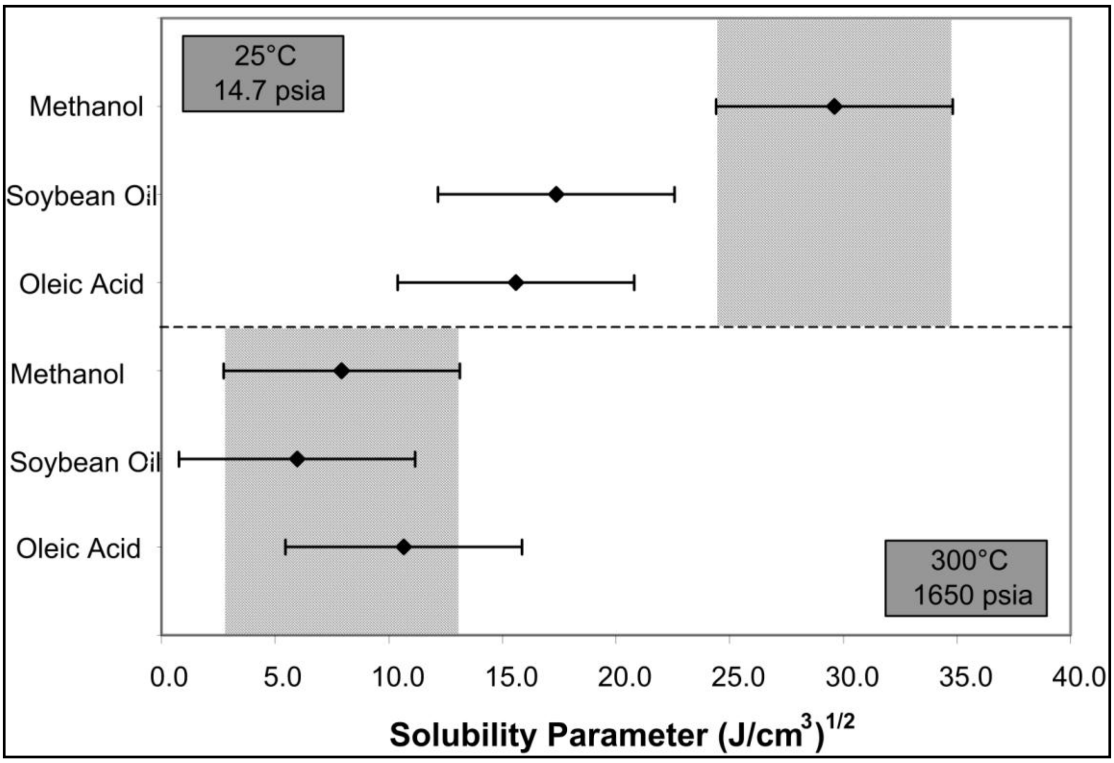


Figure 3.13 Phase diagram for methanol

Source: Schulte, 2007

A measure of a solvent's polarity, the dielectric constant of methanol also decreases in the supercritical state (Deul, 1998), which suggests that supercritical methanol behaves more like a non-polar compound (Kusdiana and Saka, 2004). This, in turn, suggests that the non-polar feedstocks for biodiesel might be better solvated in methanol in its supercritical state, greatly increasing the contact between the two. The solvent strength of methanol, and any other solvent can be quantified by its solubility parameter. There are multiple correlations for predicting the solubility parameter of a substance, such as the simple Hildebrand parameter, or the generally more accurate but more complex Hansen parameter (Hansen, 1999). The solubility parameter relies heavily on the temperature and pressure of the substance, as outlined by Schulte (2007). Table 3.3 below provides the comparison between the different substances and their solubility parameters.

Table 3.3 Comparison of solubility parameters

Substance	Temperature (C)	Pressure (bar)	Solubility parameter (J/cm^3)
Methanol	25	1	29.61
Soybean Oil	25	1	17.37
Oleic Acid	25	1	15.60
Water	25	1	47.90
Methanol	300	1	7.93
Soybean Oil	300	112	5.96
Oleic Acid	300	112	10.66
Water	300	112	27.56
Methyl Oleate	25	1	15.46
Glycerol	25	1	36.16

While maximum solubility occurs when the solubility parameter of the solute (i.e. vegetable oil or animal fat) matches that of the solvent (i.e. methanol), miscibility occurs when they are within ~5.2 (J/cm3) (Jerry, 2007). It can be observed that there is a distinct difference between soybean oil and oleic acid. This is even more evident when they are mixed with methanol in the absence of a catalyst. This difference can be attributed to their solubility parameters. For methanol, the solubility parameter is 29.6 and soybean oil and oleic acid are 17.4 and 15.6 respectively.

During supercritical conditions, methanol solubility parameter is 7.93 which is not different to that of soybean oil of 5.96 and oleic acid of 10.66. It is for this reason that the solubility between the feedstock is higher in the supercritical conditions (Schultz, 2007).

3.7 Diesel Properties

3.7.1 Cetane number

Cetane number measures the readiness of a fuel to auto-ignite the diesel engine when injected (Biodiesel Education, 2006). Cetane number defines the delay from the time when the fuel is injected into the cylinder and the time when ignition occurs. Cetane number has an effect on both compression ignition diesel and spark ignited gasoline engine. In compression ignition diesel engines, the cetane number is the measure of ignition promotion, an indication of the smoothness of combustion. In a spark ignited gasoline engine, the ignition quality of gasoline is measured by the octane number, which is a rating of ignition delay (Nash, 2000).

Nolte (2007) gave an account of the effect of cetane number on ignition. He said the higher cetane numbers indicate shorter times between injection of the fuel and its ignition. They have been associated with reduced engine roughness and with lower starting temperatures for engines. He said good ignition that results from the higher cetane numbers aid in easy starting, starting at low temperature, low ignition pressures, and smooth operation with lower knocking characteristics. He also said that low cetane fuel results in poor ignition qualities that sometimes cause misfiring, tarnish on pistons, engine deposits, rough operation and higher knocking and eventually higher noise level.

Marker and John (2006) warned of the likely confusion between cetane number and the cetane Index. They said cetane index, in general, defines the cetane number from equations that are derived for petroleum distillates. They further said that diesel that contains cetane additive, biodiesel and other fuels are not applicable to cetane index.

3.7.1.1 Impact on engine performance

There are a number of engines variable that cetane number depends on for effective performance i.e. engine capacity and design, load and speed variations, climate conditions when the engine is started. All of the above conditions play an important role in ensuring that the diesel engine starts when it is auto-ignited.

During the low air temperatures, fuels with higher cetane numbers give off less diesel knock and white smoke in the exhaust pipe. The contrary is observed with fuels of higher cetane numbers, because they have a much greater engine knock and a bigger cloud of white smoke in the exhaust pipe is observed when they are started. The above situation should not be allowed to for longer periods without any adjustments on the cetane number fuels, as there is a possibility of deposits accumulation in combustion chamber that is likely to be formed.

It is therefore, critical that the cetane number for biodiesel be maintained at 50. Biodiesel Education (2006) said that biodiesel engines may run smoothly and efficiently on cetane numbers that are lower than 50, damages on the mechanical equipment will occur after some time.

The excessive blending of diesel fuel with cetane additives should be avoided. The World Wide Fuel Charter (WWFC) recommends a difference of 3 between the cetane number and the cetane index (Nash, 2000).

The distribution and the length of the free fatty acid carbon chain in the feedstock plays an important part in the cetane number of final biodiesel produced. Van Gerpen (2005) discovered that the longer and saturated fatty acid carbon chains, will produce the biodiesel that have the higher cetane number.

3.7.2 Iodine value

To compare the chemical stability properties of different biodiesel fuels, it is desirable to have a measurement for the stability of the fuel against such oxidation as described above. Currently, the most common method for doing this, and the one specified in many of the biodiesel fuel specifications, is called the iodine number or iodine value. The Iodine Value is not determined by measuring the stability of the fuel, rather by measuring the number of double bonds in the mixture of fatty acid chains in the fuel by introducing iodine into 100 grams of the sample under test and measuring how many grams of that iodine are absorbed. Iodine absorption occurs at double bond positions. Therefore, a higher IV number indicates a higher quantity of double bonds in the sample.

Iodine numbers for some plant oils (before conversion into biodiesel):

- Coconut oil: 10;
- Rapeseed oil: 94-120;
- Soybean oil: 117-143; and
- Sardine oil: 185.

Iodine numbers after conversion to biodiesel through transesterification (approximate values):

- Rapeseed Methyl Ester (Rapeseed biodiesel): 97;
- Rapeseed Ethyl Ester (Another variety of Rapeseed biodiesel): 100;
- Soy Ethyl Ester (Soy biodiesel variety 1): 123; and
- Soy Methyl Ester (Soy biodiesel variety 2): 133.

The Iodine value can be important because many biodiesel fuel standards specify an upper limit for fuel that meets the specification.

The Iodine value (IV) does not necessarily make the best measurement for stability as it does not take into account the positions of the double bonds available for oxidation.

3.7.3 Calorific Value (Heat of Combustion)

Heating Value or Heat of Combustion, is the amount of heating energy released by the combustion of a unit value of fuels.

One of the most important determinants of heating value is moisture content. Air-dried biomass typically has about 15-20% moisture, whereas the moisture content for oven-dried biomass is negligible. The moisture content in coals varies in the range 2-30%. However, the bulk density (and hence energy density) of most biomass feedstock is generally low (between about 10 and 40% of the bulk density of most fossil fuels), even after densification. Liquid bio fuels, however, have bulk densities comparable to those for fossil fuels.

3.7.4 Melt Point or Pour Point

Melt or pour point refers to the temperature at which the oil in solid form starts to melt or pour. In cases where the temperatures fall below the melt point, the entire fuel system, including all fuel lines and fuel tank, will need to be heated.

3.7.5 Cloud Point

The temperature at which oil starts to solidify is known as the cloud point. While operating an engine, at temperatures below oil’s cloud point, heating will be necessary in order to avoid waxing of the fuel.

3.7.6 Flash Point (FP)

The flash point temperature of diesel fuel is the minimum temperature at which the fuel will ignite (flash) on application of an ignition source. Flash point varies inversely with the fuel’s volatility. Minimum flash point temperatures are required for proper safety and handling of diesel fuel.

Cetane and Iodine numbers flash and cloud points, as well as calorific value and melt point are the important parameters that determine the efficiency of the engine. However, there are other parameters that do not have an effect on the engine performance but their effect is on the environment and these parameters will be discussed below.

3.7.7 Ash Percentage

Kirshner (2005) defined ash as a measure of the metals that are contained in the fuel. Dalai, Ajay and Mangesh (2006) recommended that the concentration of Ash metals be maintained below 1ppm in the biodiesel as it can potentially result in injector plugging, deposition on combustion as well as injection system wear.

Kirshner (2005) established a relationship between the Ash content and the heating value, and she discovered that the higher Ash content results in the lower heating value.

Ash content for bio-fuels is typically lower than for most coals, and sulphur content is much lower than for many fossil fuels. Unlike coal ash, which may contain toxic metals and other trace contaminants, biomass ash may be used as a soil amendment to help replenish nutrients removed by harvest.

3.7.8 Sulphur Percentage

Sulphur percentage is the percentage by weight, of sulphur in the fuel.

3.7.9 Potassium Percentage

Potassium percentage is the percentage by weight, of potassium in the fuel.

CHAPTER 4

SELECTION OF CONVERSION PROCUDURE

4.1 Introduction

In the previous chapter, various conversion procedures were described. This Chapter will discuss the selection of a conversion procedure. Firstly, the Chapter will describe the criteria that were used to select the conversion procedure. Secondly, it will then discuss the reasons why each conversion procedure was selected or not selected.

4.2 Selection of conversion procedure

There were a number of conversion procedures that were considered for this application as discussed in the previous Chapter. These procedures have been traditionally used to convert vegetable oil and spent cooking oil into biodiesel with much success over the years. Most of these feedstocks would contain mostly triglycerides and small amounts of free fatty acids, which made conversion easier. However, due to the high amount of free fatty acids in both our feedstocks, using these procedures was found to be inappropriate (Schulte, 2007). A criteria was then developed that was used to select the best possible procedure and it was based on the following categories that are described below:-

- Reaction conditions (temperature and pressure);
- Reaction time;
- Ability to convert free fatty acid into alkyl esters;
- Yield;
- Availability of the raw material;
- Complexity of the process;
- Catalyst requirement; and
- Pre-treatment requirement the conversion process.

4.2.1 Base Catalysed transesterification

This conversion procedure was found to be inappropriate for the tall oil fatty acid and crude tall oil because of the high free fatty acid content of the feedstocks. The long reaction times and low yield that are caused by the high free fatty acid content made this procedure to be inappropriate for this conversion.

The requirement of a catalyst increases the cost of the conversion costs and the process is also complex because there is soap that is formed at the end of the reaction time which makes separation difficult due to the saponification reaction that takes place.

4.2.2 Acid Catalysed esterification

This conversion procedure was also found to be inappropriate for this study because the reaction time is longer. The major problem with this procedure is the catalyst separation and recovery, the removal of water to drive the reaction to completion which if it did not happen, could result in incomplete reaction. It is also not a safety procedure because the catalyst that is extensively used is a highly concentrated sulphuric acid.

4.2.3 Enzyme Catalyst

This conversion procedure could have been an interesting procedure to evaluate, but the supplier that the researcher contacted did not have a product in stock. The lead time was 4 months and this would not have given the researcher enough time to complete the study. The fact that there is no by-product formation (including soap) and the catalyst recovery is simple makes this procedure attractive. There are, traditionally challenges with the use of enzyme that the researcher was aware of them, e.g.

- High costs of the enzyme (quoted at R25 000/kg, but the dosage is small to compensate for the high cost); and
- Instability (they easily become inactive).

This conversion procedure would be recommended for future studies as there are reported successes; especially with the feedstocks of higher free fatty acids content.

4.2.4 Hydroprocessing

This conversion procedure was also found to be inappropriate for the biodiesel production because of the by-product formation like water, light hydrocarbon and some heavier hydrocarbons that require separation from the final biodiesel product. These by-products reduce the yield and the efficiency of the process because removing them require costly operation like distillation, amine absorption and pressure swing adsorption.

There is also another disadvantage with these procedures because there is a separate isomerisation step that is required to improve cold-flow properties. Also, the feedstock require pre-treatment to prevent impurities from poisoning the catalyst.

4.2.5 Supercritical Methanol treatment

This conversion procedure was chosen for this study above the rest of the procedures that have been discussed. Supercritical methanol treatment requires no pre-treatment of the feedstock. The additional of methanol, which promotes the nucleophilic attack of methanol on the carboxyl groups in the feedstock, increases the reaction rates of esterification or transesterification.

This procedure has a short reaction time because it attacks the free fatty acids and triglycerides directly. Also, there is no separate catalyst for biodiesel production and, hence, no need to recover or regenerate the catalyst. This is the distinct difference with the other procedure as there is no consumption of the catalyst by free fatty acids.

There is also no formation of emulsions resulting from water. The reaction is also not retarded by water as was evident with the other procedures

4.3 Summary

This Chapter discussed the criteria that were used to select the conversion procedure for tall oil fatty acids and crude tall oil into biodiesel. Base acid transesterification, acid catalysed esterification, enzyme catalyst, hydroprocessing and supercritical methanol treatment method were discussed as the possible conversion procedures. Based on the quality of the feedstock, it was concluded that supercritical methanol treatment will be suitable for this study.

CHAPTER 5

EXPERIMENTAL PROCEDURE

5.1 Introduction

This chapter will discuss the experimental procedure that was followed during this study. The Chapter will begin by describing the apparatus that was used during the study. This will include the features of the testing equipment and operating variables. Secondly, the Chapter will also discuss the procedure that was followed when charging the reactants into the reactor. Thirdly, the Chapter will then discuss the procedure that was followed when analysing the parameters of the biodiesel final product. Fourthly, the Chapter will discuss the sourcing of the feedstocks.

Safety consideration during the study will also be discussed.

Due to the unavailability of certain laboratory equipment, samples were sent to the external laboratories for the following analysis:-

- Cetane and iodine values; and
- flash, cloud, and melting points.

However, the procedures that were followed during their analysis will also be discussed.

5.2 Apparatus

Equipment used for this study was the pressure vessel that was borrowed from Sanikwa Biodiesel Centre. Below is a schematic diagram for the supercritical methanol reactor that was used.

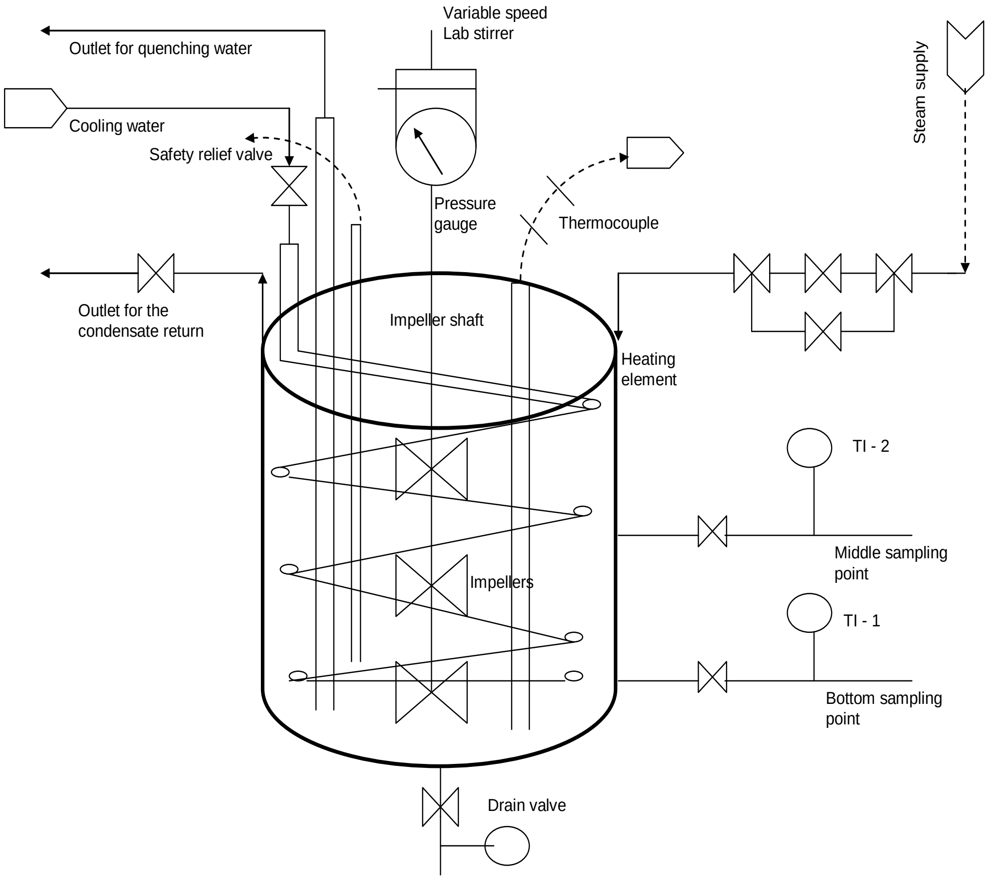


Figure 5.1 Schematic diagram for the Supercritical Methanol reactor

5.2.1 Range of variables investigated

Table 5.1 below depicts the process variables that affect the supercritical methanol procedure as listed by Lin and Wai (2003).

Table 5.1 – Range of variables investigated

Variable	Symbol	Units
Pressure	P	Kpa
Temperature	T	C
Methanol to feedstock ratio	Me: OH	
Time	t	minutes

Lin and Wai (2003) have identified the reaction temperature and feedstock to methanol ratio as the two most critical variables for the effective conversion. Their impact on the overall costs of production is noted especially when the procedure has to be conducted on a plant-scale with supercritical methanol treatment.

Optimization of these parameters will have the following effects:

- minimum requirement for the necessary energy for heating the reactants;
- methanol requirements will be lower;
- separation requirements will be lessened;
- reactor volumes will be minimise; and/or
- production rates will be increased.

Using the study that was performed by Kusdiana and Saka (2001), the following range of parameters were determined for this study and are indicated in Table 5.2.

Table 5.2 – Testing conditions for supercritical methanol method

Parameters for the Experiment	Testing Conditions
Reaction Time	10 - 40 minutes
Reaction Pressure	113 bar
Reaction Temperature	250 – 350°C
Methanol to Feedstock Ratio (mol/mol)	10 - 40

In-order to understand the effects of temperature and pressure only, for the first part of the study - reaction time and pressure were held constant at 113 bar and 20 minutes respectively. It should be noted that this pressure is above the critical pressure of methanol P = 135 bar), and it was the highest rated pressure of the batch reactor. The study used pressure of 113 bar, which is slightly below the other studies that were found during literature survey on supercritical methanol treatment. However, this pressure would be more practical in an industrial scale.

The temperature of the reaction was kept in the range of 250 - 350°C, which is the favourable condition for the supercritical methanol treatments. This range is still below the thermal degration levels.

A range of 10:1 and 40:1 for the methanol to feedstock ratio was used for the study. This range was selected based on the previous studies conducted with supercritical methanol treatment as explained in Chapter 3.

5.3 Experimental Parameter Testing Conditions

P-V-T Modelling

In order to determine the proper amount of reactants required to charge to the reactor, the Peng-Robinson equation of state, commonly used for supercritical systems, was chosen to predict the pressure of the system:

$$P = \frac{RT}{(V - b)} - \frac{a(T)}{(V + \varepsilon B)(V + \sigma b)} \ldots\ldots\ldots\ldots\ldots(1)$$

Equation 1 - Generalized cubic equation of state

where: *R* is the universal gas constant (bar mL mol^{-1} K^{-1}),

T is the reactor temperature (K),

V is the specific volume of the reactor contents (mL mol^{-1}), and

a(T), and *b* are parameters that are equation of state and compound specific.

For multi-component systems, *a(T)* and *b* are mixture parameters that are functions of composition. Since no established theory describes this relationship, empirical mixing rules are used to relate the pure-species parameters to the mixture parameters. For *i* components, a linear mixing rule was applied to parameter *b*:

$$b = \sum x_i b_i \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Equation 2 - Linear mixing rule for the multi-component b-parameter

and a quadratic mixing rule was applied for parameter *a*:

$$a = \sum_i \sum_j x_i x_j a_{I,i} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Equation 3 - Quadratic mixing rule for the multi-component a-parameter

where: x is the mole fraction of a species, and

$a_{i,j}$ is an interaction parameter, evaluated by a geometric mean rule:

$$a_{i,j} = (a_i a_j)^{1/2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(4)$$

Equation 4 - Geometric-mean combining rule

The interaction parameters are computed from the pure-species parameters:

$$a_i(T) = \psi\ \alpha_i \frac{(T_{r,i})R^2T^2_{c,i}}{P_{c,i})} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

Equation 5 - Pure-species a-parameter

$$bi = \Omega\ \frac{RT_{c,i}}{P_{c,i}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

Equation 6 - Pure-species b-parameter

where: T_c,i is the critical temperature of component i (K),

P_c,i is the critical pressure of component i *(bar)*,

ψ α and Ω are parameters that are equation of state and compound specific

Table 5.3 - Peng-Robinson equation of state parameters

Equation of State Parameter	Peng-Robinson Values
Є	$1 - \sqrt{2}$
σ	$1 + \sqrt{2}$
Ψ	0.45724
A	$[1+(0.37464+1.54226\omega-0.26992\omega^2)(1-T^{1/2})]^2$
Ω	0.07779

Peng-Robinson equation of state (PE-EOS) is used to determine the appropriate charge of reactants in the reactor. The use of this technique is based on the assumption that under supercritical conditions of methanol, a well-established single fluid phase would be formed, with which the PE-EOS has been shown to be fairly accurate.

5.4 Procedure

This section describes the procedures that were followed during the study, from charging reactants into a reactor, reactor set-up, and supercritical methanol method through to the final product analysis.

5.4.1 Procedure for Charging Reactants to the Reactors

Figure 5.4 below is a flow sheet that was designed and followed during the charging of the reactants into a reactor.

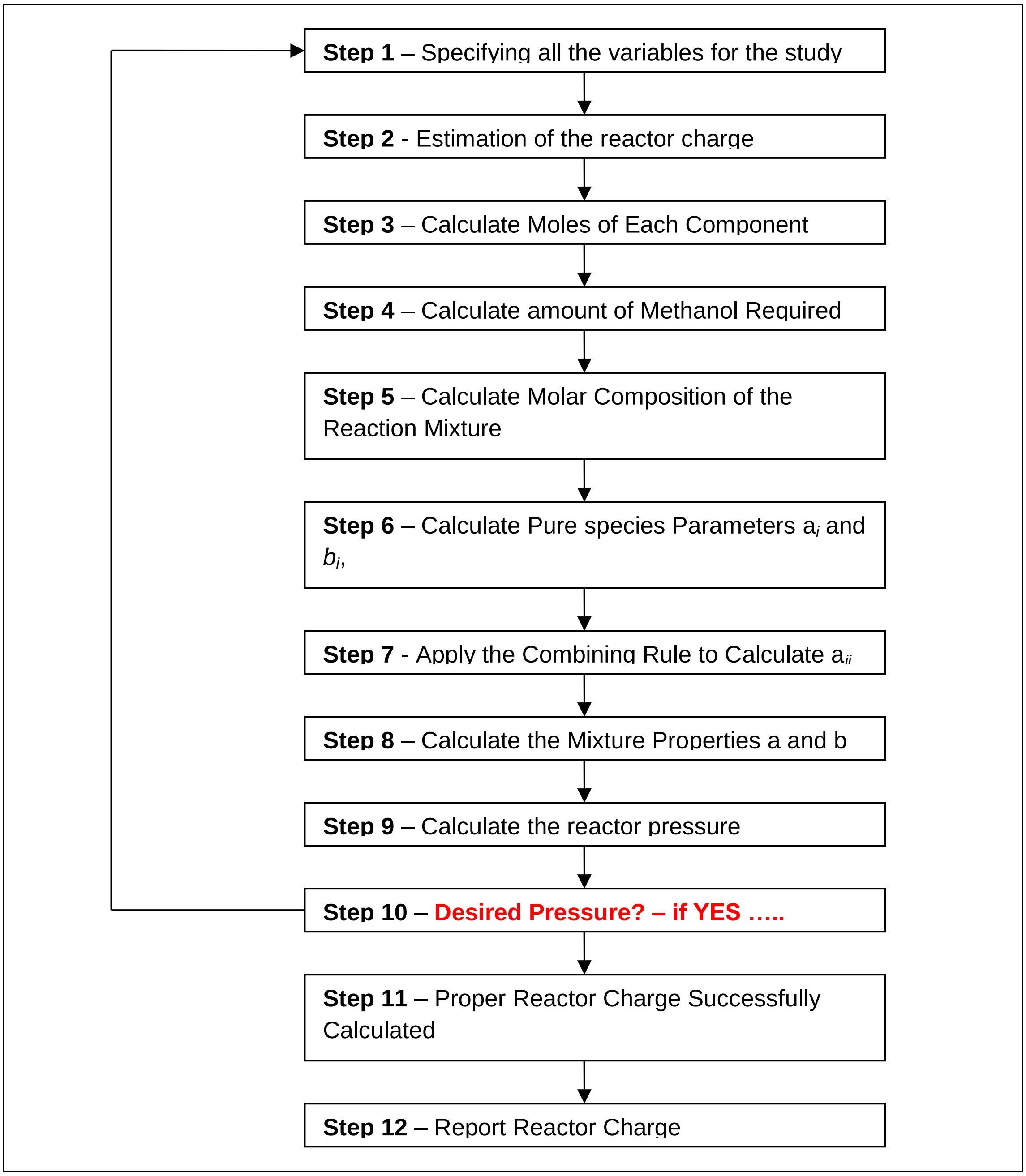


Figure 5.2 – Flowsheet for calculation of the proper charge to the reactor

The reactor volume was specified along with the reaction temperature, methanol to feedstock ratio and feedstock composition for the particular temperature. The concentration of feedstock was determined, as were the molar amounts of each component to be used for the reaction.

The above, enabled a methanol to feedstock ratio determination to be performed. On an equal mass basis with respect to the sample charge, the amount of deionised water needed was calculated. The molar fraction of each component (x_i) in the reaction mixture was also calculated. The pure-species parameters, a_i and b_i, was calculated using Equation 5 and Equation 6, respectively. The interaction parameters ($a_{i,j}$) was calculated from the pure species parameters using Equation 4. The mixture parameters, b and a, was calculated from Equation 2 and Equation 3, respectively. Finally, the reactor pressure was calculated using Equation 1.

By varying the reactor charge, steps 3 through 10 were repeated until the reactor pressure converged to the desired value of 113 bar. There was a discrepancy in the calculation on some of the temperature and feedstock: methanol ratios which could be attributed to the possible presence of two phases.

5.4.2 The Supercritical Methanol Treatment Method

Due to the nature of the feedstock, a portable stirrer was used to ensure that crude tall oil was always in suspension and did not separate. The feedstock was then poured into a 5-litre bucket which was used as temporary storage for the stirred feedstock. The feedstock was then scooped out of the 5-litre bucket and transferred into a 500 ml beaker. The sample was heated up to 60°C to ensure the easier transfer of the feedstock and to improve the viscosity of the feedstock.

After determining the amount of feedstock to be added, the correct amount was weighed in a 200 ml graduated cylinder. After untightening the screws and opening the top of the reactor, the feedstock was then poured into an already stirring tank reactor. Care was taken to ensure that all feedstock poured into a cylinder was poured into the reactor. The quantities of the feedstock that was left in a cylinder was weighed and noted, so that the residue would be considered when calculations, especially for the yield, are performed. Similarly, water and methanol mass were weighed in a graduated cylinder and poured into a reactor. The reactor was then closed and top screws tighten.

The reaction vessel was then placed in a Parr Instrument 1, 500W and 115-volt Calrod heater assembly. The heater was connected to a VAC rheostat. At this stage, the reactor was secured to the heater, which was in turn bolted to the ground with concrete anchors. A supply line for cooling water was connected to the coil inlet by ¼” stainless steel tubing, fed by ¼” thermal resistant tubing, which in turn was fed by ¼” braided PVC tubing. This arrangement made sure that no leaks could develop in the cooling system if there was thermal degradation of the tubing materials in close proximity to the reactor. A ball valve was used to control the flow of water.

A supply line of cooling water was circulated through the magnetic drive’s sleeve assembly with the rheostat setting set to 100% and the motor was turned on to provide agitation. This start time was noted. The reaction temperature was monitored over time until the desired condition was reached, and again, the time that this took, was recorded. Previous testing with water allowed for sufficient manual control of the temperature by adjusting the rheostat. The actual reactor pressure was recorded so that it could be compared with the expected or theoretical pressure. The rheostat was adjusted to maintain the desired temperature. These conditions were held for a specified reaction time of 20 minutes. At the end of the specified reaction time, the rheostat was turned off and the cooling water valve opened. The reactor was allowed to cool until it was safe to handle and the rate of cooling was recorded. Any excess pressure was released by opening the gas release valve.

After disconnecting the cooling water lines and removing the motor assembly, the reactor was retrieved and the head assembly was removed, as outlined previously. The reactor contents were then poured into a 1,000 ml sample container.

5.4.3 Product Analysis

After the reaction, the contents of the reactor were mostly biodiesel, unreacted methanol as well as feedstock. The separation of these products was enhanced by their densities which were distinctly different. The contents were kept in a 1 litre container for about 12 – 14 hours to aid separation of these components.

Two phases were observed in the funnel i.e. the top and bottom phases. The bottom phase was mainly water and methanol, and the upper phase was mainly biodiesel, excess and unreacted methanol as well as free fatty acids. The top phase of the funnel was transferred into a 500 ml beaker, where it was weighed. Both the top and bottom phases were distilled for an hour at 90C. Also, the unreacted methanol was collected and weighed.

It was noticed from the visual appearance that there was unreacted Crude Tall Oil and Tall Oil fatty acids in the biodiesel. Distilled water of between 20 – 40ml was added into biodiesel in a separate funnel. The mixture was vigorously mixed and settled for 12-hours. The top section of the funnel which was collected was then weighed and the bottom section which was mostly unreacted product was removed.

5.4.4 Unreacted Reactants in the Final Product

As indicated above, the reactor had both the final biodiesel products as well as unreacted reactants. The mixture was allowed to settle in a funnel. Also, the two phases were noticed i.e. the top and the bottom phases. The upper phase consisted of mostly biodiesel. There was also excess methanol and unreacted free fatty acids. The top phase was distilled for 1 hour at 90C to remove excess methanol and free fatty acids were removed from the final biodiesel products by titrating with sodium hydroxide below a pH of 8.5. Soaps from the saponification of free fatty acids were produced from titration, which were centrifuged for 12 hours. From this phase, water and soaps were easily removed because they were denser. The top phase which was the final biodiesel product, was collected and weighed.

5.5 Biodiesel Parameter Measurements

5.5.1 Ash

The method used for determination of the Ash was based on TAPPI Test methods – T413 0m-93. This method involves igniting the test specimen in a muffle furnace at 900°C and then analysing the product for ash percentage. Ash on the material remaining is calculated on the basis of the dry weight of the original sample after the sample is ignited at the specified temperatures. The apparatus used for these tests were 50 ml crucibles with covers.

5.5.2 Viscosity

The method used for the determination of the viscosity was determined from TAPPI Test methods – T230 0m-94. The viscometer was placed on a flat surface. The sample was poured into a 500ml beaker until the reading on the beaker reached approximately 350ml. The spindle was attached onto the shaft of the viscometer. Care was taken to ensure that speed did not exceed 100 at any time. The spindle was inserted into the sample until the mark or groove was reached (done by turning the knob on the right of the instrument). The gear lever was depressed and the motor switched "ON". After ±5 seconds, the gear lever was released and the spindle rotated in the liquid. After 30 seconds, the gear lever was depressed and the motor was switched off in such a manner that the reading could be obtained. The reading was taken and the temperature obtained with a thermometer – TEC. Using the Model Number, Spindle Number and speed to obtain the factor (by which the reading must be multiplied) from the provided sliding chart, the viscosity was calculated as:

$$\text{Viscosity @ TEC (cps)} = \text{Factor x Reading}$$

5.5.3 Acid Number

The method used for the determination of the acid number was found from TAPPI Test methods – T689 0m-93. About 1 to 2 grams of well mixed sample was weighted off accurately into a 250 ml beaker. (M – gram). A mixture of 100 ml of methanol/xylene was added into a weighed sample and was swirled and allowed to dissolve. A pH electrode was immersed into the dissolved sample and was then titrated with 0.5N alcoholic potassium hydroxide until a pH of 10.7 was obtained. The titrant volume (V – ml) was recorded. Care was taken to ensure that the pH electrode was positioned to avoid damaging it with the magnetic stirrer. The titrant was slowly added near the point and the acid number became:-

$$\text{Acid number} = \frac{V \times N \times 56.1}{\text{KOH/g oil}}$$

Where N is the normality of the alcoholic KOH

5.5.4 Cetane and Iodine Numbers

Samples were sent to an external laboratory for analysis to determine the cetane and iodine numbers.

5.5.5 Melting, Boiling and Flash Points

The final samples of biodiesel were given to Buckman Laboratories, who assisted during the study with the determination of melting, boiling and flash points.

5.6 Feedstock sourcing

The objective of the study was to evaluate the feasibility of converting crude tall oil and tall oil fatty acids into biodiesel. Crude tall oil was the first feedstock considered. This is the by-product of the papermaking process as described in Chapter 3 and it was readily available at Sappi Tugela. .

The second feedstock was the tall oil fatty acids, which was purchased from Protea Chemicals in Jacobs. As it was explained in Chapter 2, this feedstock is a largest component of Crude Tall Oil. The Mill sells Crude Tall Oil into a third party, and the product undergoes a fractionating process to separate all major three components i.e. tall oil fatty acids, pitch and rosin. The party then distributes the components for Commercialisation to Protea Chemicals and other specialty chemicals distributors around the country.

Based on the GC Scan of the crude tall oil that was performed on the sample, the following values are reported below in Table 4.1:

Table 5.4 – Concentration of components in the CTO

Component	Concentration (mass %)
Paltimic acid	12.0
Oleic acid	34.7
Linoleic acid	37.3
Total	84.0

Figure 5.1 below is a GC-Scan of the crude tall oil and the biodiesel sample purchased from Engen Service Station in Willow Stuck Road. The sample in white illustrates the crude tall oil and the green represents a biodiesel sample. Both these two samples were analysed under the same conditions. From the chromatogram of the biodiesel sample (green) it is possible to see C14-C24 methyl esters. From the tall oil (white) sample it is clear that no methyl esters such as in the biodiesel is observed, but rather the acids C17 (paltimic acid) and C18 (oleic and linoleic acid) are the major components present in the sample.

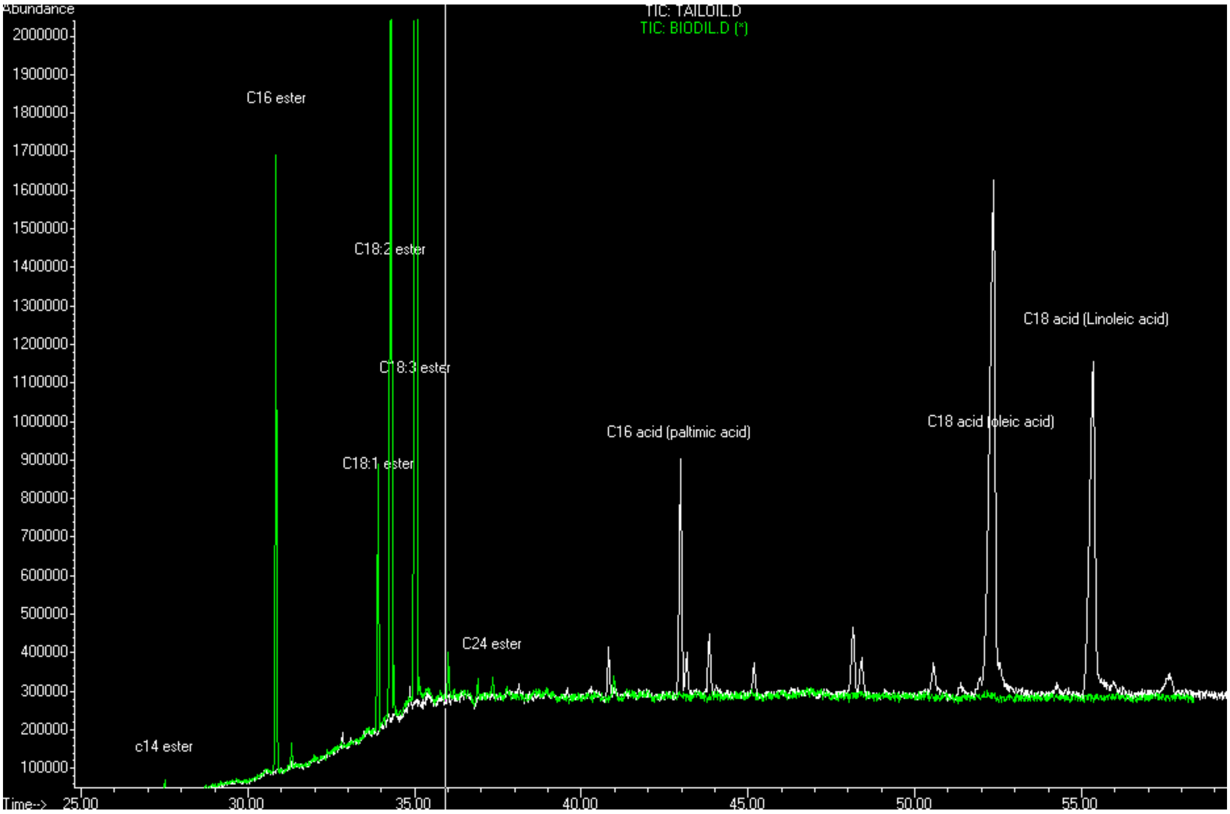


Figure 5.3 – GS Scan for the CTO sample

5.7 Safety consideration during the study

During the laboratory work, standard personal protective equipment was worn at all times. This was to ensure that the potential risk, especially with methanol handling, was reduced. The following personal protective equipment was worn by the researcher during the study:-

- long pants;
- safety glasses;
- acid resistant gloves;
- steel toed shoes; and
- laboratory coat.

5.8 Summary

This Chapter discussed the experimental procedure that was followed during the study. It began by describing the equipment that was used, range of variables investigated and the procedure that was followed to charge reactant into the reactor.

The analysis of the final products was discussed in this Chapter. The procedures that were used to test biodiesel parameters were also discussed in this Chapter.

The sourcing of the two feedstocks used for the study was discussed and the reasons for purchasing tall oil fatty acids from the third party were provided.

Lastly, the safety precautions and considerations during the study, to ensure that the investigation happened without any safety incidents were discussed.

CHAPTER 6

RESULTS AND DISCUSSIONS

6.1 Introduction

The objective of the study was to evaluate the feasibility of converting the tall oil fatty acids and crude tall oil into biodiesel. This Chapter presents and discusses the results in the following sequence for both the feedstocks:-

- repeatability of the results;
- effect of time on biodiesel yield;
- effect of methanol: feedstock on biodiesel yield; and
- effect of temperature on biodiesel yield.

Also, this Chapter presents the results of the biodiesel parameters that were achieved during the experiment work which are divided into performance and environmental indicators.

Finally, the Chapter presents a comparison of the biodiesel products that were produced from both the feedstocks.

6.2 Validity

Validity refers to the extent to which a specific test measures exactly what it claims to measure, whereas reliability refers to the extent to which the results achieved when the same tests conducted are consistent (Bryman and Bell, 2007).

Figure 6.1 below shows the data collected for the two experiments that were repeated at a temperature of 325°C, 20 minutes reaction time and different methanol to feedstock ratio.

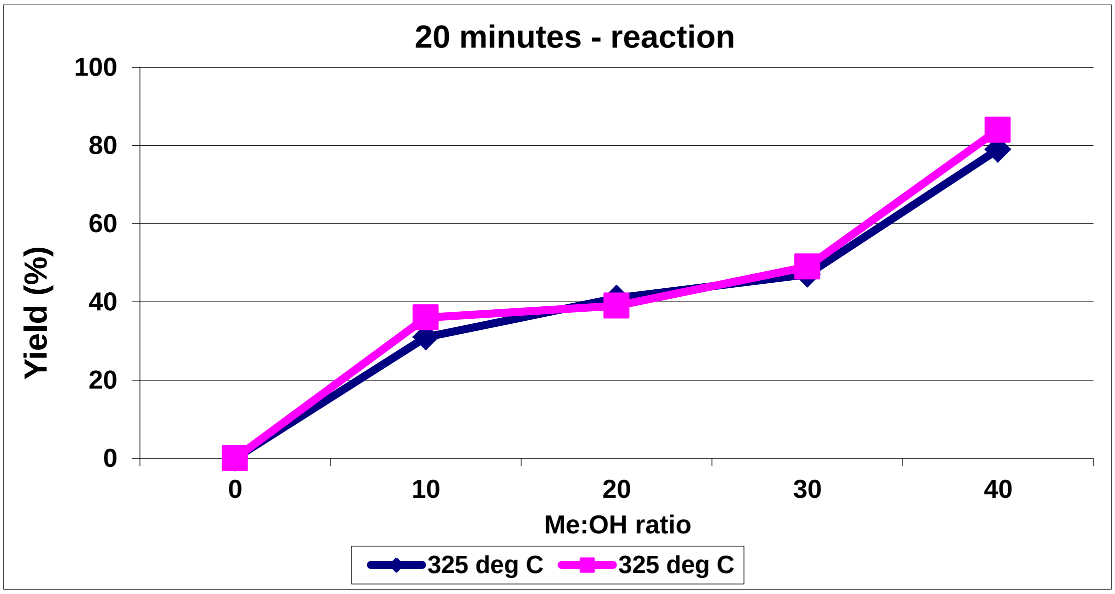


Figure 6.1 – Repeatability and validation graph

There is a relative deviation from the mean value range of between 2 and 4%. It can therefore be concluded that the repeatability and the validity of the data that was collected during the study were good.

6.3 Conversion of Tall oil fatty acids

This section presents the results that were achieved when the feedstock was tall oil fatty acids. There are three parameters that will be presented and their effect will be considered against the biodiesel yield that was achieved.

6.3.1 Effect of time on biodiesel yield.

Figure 6.2 represents the effect of time on biodiesel yield across different temperatures when tall oil fatty acids were used as a feedstock.

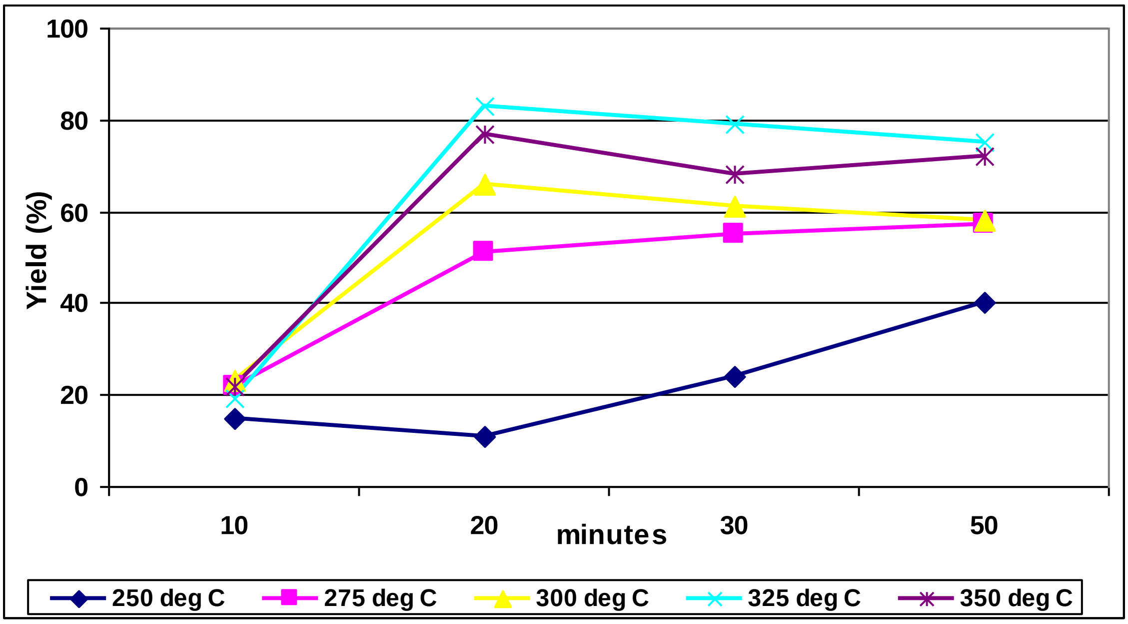


Figure 6.2 – Effect of time on biodiesel yield (10, 20, 30 and 50 minutes)

From the above figure, there was an increase in biodiesel yield from 10 to 20 minutes reaction time, and there was a reduction from 20 to 30 minutes for a reaction temperature of 300°C, 325°C and 350°C. A different trend was observed with the 250°C, where there was a slight decrease of biodiesel yield from 10 to 20 minutes. Also, for 20 to 30 minutes reaction time, an increase in biodiesel yield was observed as well as for 30 to 50 minutes reaction time. A similar trend was observed for 275°C reaction temperature, where biodiesel yield increased when the reaction time increased to 20 to 50 minutes.

When the reaction time increased from **10 minutes to 20 minutes**, the biodiesel yield was increased to 83% at 325°C. For the experiment samples that were heated up to 275°C and 300°C, there was increase to 51% and 64% respectively at the reaction time of 20 minutes. These yields were the highest that were achieved during the experiments. For the temperature at 350°C, which was the highest temperature for the experiment, the biodiesel yield was 79% for the reaction time of 20 minutes.

For the **30 minutes reaction time**, the highest biodiesel yield was 79% and this was achieved at 325°C. The lowest yield was achieved at 40% for the sample that was heated up to 250°C. Yields of 56% and 60% was achieved for the samples that were heated up to temperatures of 275°C and 300°C respectively.

For the **50 minutes reaction time**, the highest yield of 75% was achieved at 325°C. The lowest yield was achieved at 40% at a temperature of 250°C.

The highest yield of 83% was achieved at 20 minutes reaction time. These results are consistent with the study done by Schulte (2007) with the supercritical methanol treatment on chicken fat. In his study, the yield on a 60 minutes reaction was found to be 83.6%, whereas that of the 20 minutes reaction (all else equal) was found to be 78.9%. He concluded that though there was an increase in biodiesel yield (4.7%) after tripling the reaction time, it did not justify operating the supercritical methanol treatment above 20 minutes. Schulte further said that the results suggested that the reaction time might be optimised based on the yield and process throughout. Such optimisation could increase productivity and decrease downstream processing requirements.

6.3.2 Effect of methanol: tall oil fatty acids on biodiesel yield

Figure 6.3 indicate the yield of biodiesel over a range of methanol to tall oil fatty acid ratios across different temperatures that were measured.

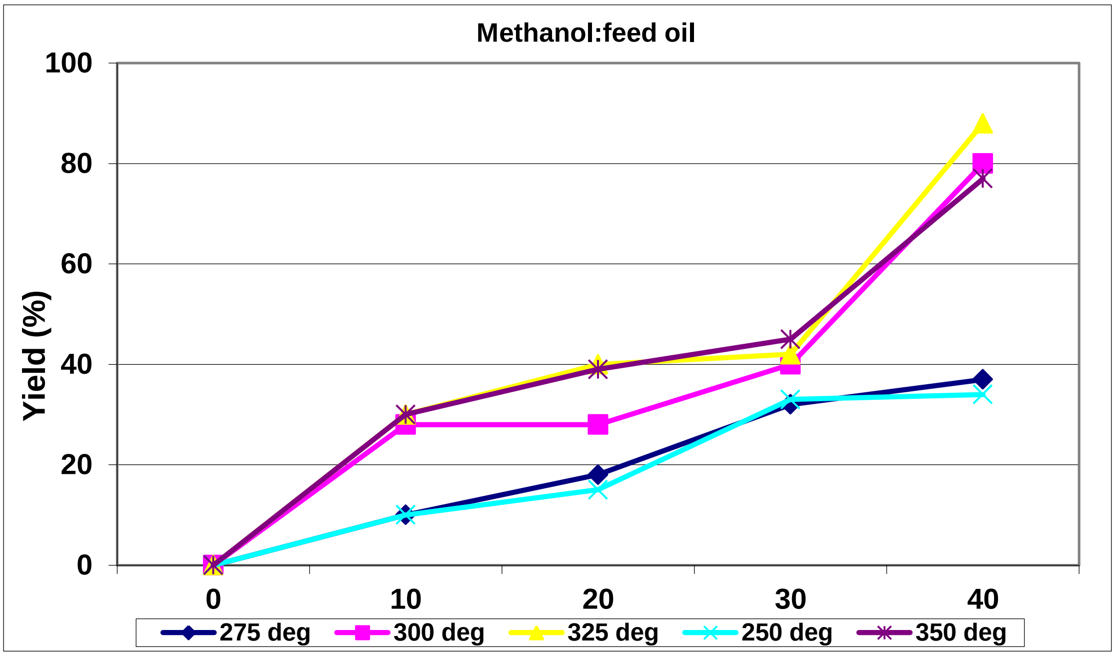


Figure 6.3 – Effect of Methanol: TOFA ratio on yield

From the figure above, it can be observed that there is an increase in biodiesel yield as the methanol to tall oil fatty acid ratio increases.

When the methanol to tall oil fatty acids increased from 10:1 to 20:1, the biodiesel yield increased from below 10% to 30% for the reaction temperature 300°C, 325° and 350°C. This was observed for all of the different temperatures tested. A similar trend continued to be observed that when the methanol to tall oil fatty acid ratio increased, the yield increased. There was, however, a steep increase to above 80% when the ratio was at 40:1 for 300°C, 325°C and 350°C. This sudden increase can be attributed to the fact that the reaction was approximately complete at a temperature of 325°C.

Though there was an increase in biodiesel yield at 40:1 methanol to tall oil fatty acids for 250°Cand 275°C, the increase was not as steep. The maximum biodiesel yield achieved at this ratio was 38%.

This is consistent with other studies conducted with the other types of oil. Schulte (2007) investigated the supercritical methanol treatment for different types of oil including chicken fat and found that above the ratio 30:1, the methanol acts as an acidic catalyst which results in the increase in biodiesel yield.

Schulte (2007) also gave an account of the increase in biodiesel yield that, as the methanol to tall oil fatty acid ratio increases, there is an increased probability that a free fatty acid will make contact with a methanol molecule to support the esterification process. An increase in methanol concentration also helps repress the reverse hydrolysis reaction of biodiesel (methyl esters) and water to free fatty acid and methanol.

Kusdiana and Saka (2001) utilized a batch reactor to transesterify oil triglycerides from rapeseed with methanol at temperatures ranging from 350°C to 400°C and pressures ranging from 113 bar to 131 bar respectively. These conditions are similar to this study. The reaction took 4 minutes of supercritical methanol treatment and the resulted in a 95% conversion of rapeseed oil to methyl esters. The reaction time was the fastest at 4 minutes compared to 1 hour for the conventional catalysed methods. There was also another advantage that they cited, in that there was no soap formation or catalyst recovery procedure involved and the separation of the product was easier at the end of the reaction.

They subsequently adjusted molar ratios of feedstock to methanol, and at 42:1, a complete conversion was found after 5 minutes, whereas with a ratio of 3,5:1 and at the same treatment time, the yield of methyl esters dropped to 55%. The results indicated that higher molar ratios of methanol resulted in a more complete transesterification reaction. This finding is consistent with the result of this study.

6.3.3 Effect of temperature on biodiesel yield

Figure 6.4 indicates the effect of temperature on biodiesel yield across different methanol to tall oil fatty acids ratios.

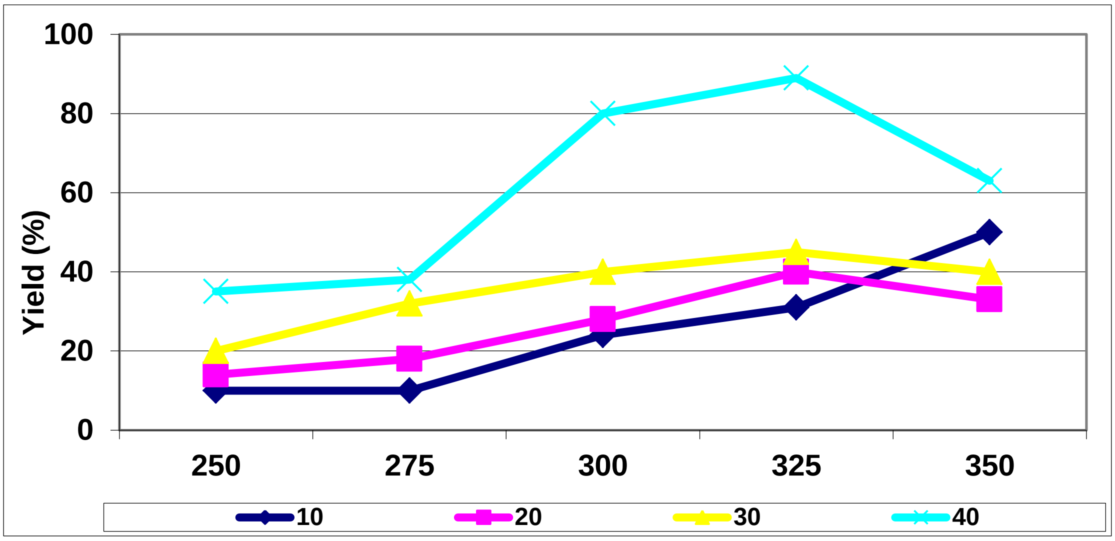


Figure 6.4 – Effect of temperature on biodiesel yield

An increase in temperature up to 325°C resulted in an increase in biodiesel yield. At a temperature of 250°C, a yield of 20% was observed for all ratios. At 275°C the yield was between 32 – 38% for the 20:1 and 30:1 and when the temperature was increased to 300°C, the yield was 80% for the 40:1. At a temperature of 325°C, the highest yield of 89% was obtained at a methanol to tofa ratio of 40:1.

At lower temperatures below 300°C, the conversion of feedstock to biodiesel was low and the reaction time is long. This could be attributed to the subcritical state of methanol. Also, at this low temperature the supercritical state is unstable. At a temperature above 325°C, thermal degradation was found to take place, defining an optimal temperature range for supercritical treatment of between 300°C and 350°C.

During a study that was done by Kusdiana and Saka (2001), a similar trend was obtained with the methanol to tall oil fatty acids of 40:1. They used chicken fat and observed that the yield dropped from 89% to 86% at a temperature of 350°C. They also found that the low conversion obtained at low temperature, 275°C, could be attributed to the presence of multiple phases due to the instability of the supercritical state. They concluded that, depending on the feed oil, a vapour/liquid two phase system can still exist up to a temperature of 290°C. There was, however, a strong correlation between single – phase formation and biodiesel yield.

This was also consistent with the test results achieved by Schulte (2007) when he also used chicken fat. He supported the potentially important role of phase behaviour of the supercritical reaction, as opposed to the effect of temperature.

The incremental yield of biodiesel between 275°C and 300°C (subject to temperature and phase differences) is greater than that between 300°C and 325°C (subject to temperature differences only).

The successful results achieved at 300°C and 325°C attest to that results obtained, that suggested that, the higher yields are achieved at elevated reaction temperatures.

6.3.4 Biodiesel parameters

Below are the acceptable ranges of biodiesel as provided by the Engine Manufacturers Association (South African Petroleum Industry Association, 2006).

Table 6.1 Biodiesel specification

Property	Limits	Units
Flash point	101 - 230	°C
Iodine number	95 - 105	
Viscosity, 40°C	3.5 – 5.0	Mm2/s
Cetane number	>50	
Density	860 - 900	Kg/m3
Acid Value	0.5 max	Mg KOH/g
Ash percentage	<0.01	ppm
Sulphur percentage	<0.01	ppm
Potassium percentage	>1	ppm

Table 6.2 illustrates the results of the biodiesel parameters that were achieved when tall oil fatty acid was used as a feedstock. The final biodiesel product was tested for both the performance and environmental indicators. **NB** – the blue colour on values in the table below indicates the out of range values.

NB – the following analysis were conducted with the biodiesel produced at 20 minutes

Table 6.2 – Biodiesel Parameters (250°C and 275°C)

Perfromance indicators								
	250 deg C				**275 deg C**			
Feed stock: methanol	10	20	30	40	10	20	30	40
Melting point	-8	-5	-8	-4	-7	-3	-10	-6
Flash point	150	165	180	220	145	175	201	190
Iodine number	103	100	**112**	106	99	**112**	103	102
Viscosity	3	**6**	4.6	4.9	5	4.9	**5.8**	**6**
Cetane number	52	51	56	58	56	51	54	60
Density	890	**970**	910	880	870	910	960	910
Acid value	0.23	0.09	0.36	0.43	0.41	0.45	0.47	0.46
Environmental indicators								
Ash percentage	0.009	0.01	0.007	0.01	0.0009	0.007	0.007	0.01
Sulphur percentage	0.0015	0.0007	0.0007	0.0009	0.02	0.008	0.01	0.003
Potassium percentage	2.5	4	6	7	5	8	3	5

Table 6.3 – Biodiesel parameters (325°C and 350°C)

Performance indicators								
	325 deg C				350 deg C			
Feed stock: methanol	10	20	30	40	10	20	30	40
Melting point	-6	-4	-3	-3	-3	-6	-4	-10
Flash point	170	160	220	180	190	160	220	180
Iodine number	95	**110**	**108**	**110**	88	102	**110**	**110**
Viscosity	4.6	5.8	**6.1**	**7.3**	**5.5**	**7.1**	**6.4**	**7**
Cetane number	60	50	54	66	**49**	55	61	67
Density	890	**840**	930	900	880	900	870	900
Acid value	0.4	**0.59**	0.47	0.5	0.43	**0.7**	**0.61**	0.46
Environmental indicators								
Ash percentage	0.001	0.005	0.007	0.003	0.0007	0.006	0.008	0.01
Sulphur percentage	0.04	0.004	0.05	0.02	0.009	0.08	0.004	0.004
Potassium percentage	2	6	4	6	7	5	9	11

Performance and Environmental parameters indicated that the biodiesel produced could be used because it met most of the specifications that are set out by Engine Manufacturers Association.

6.3.4.1 Viscosity

Figure 6.5 below represents the viscosities that were measured from the biodiesel produced when the feedstock used was tall oil fatty acid. These viscosities were measured at different temperatures as indicated below.

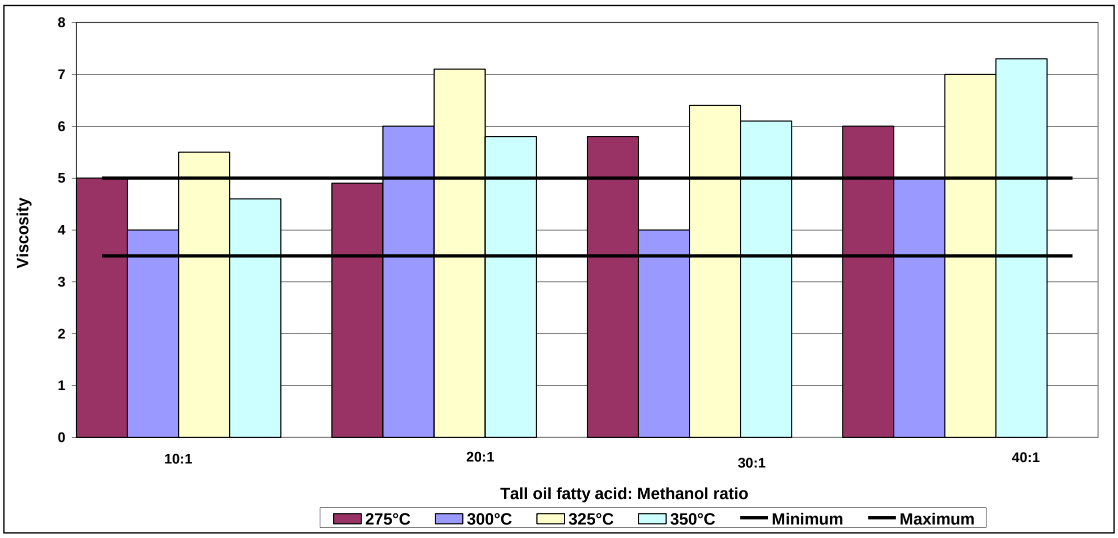


Figure 6.5 – Viscosity (TOFA)

It can be observed from the figure above that a correlation existed between the viscosities achieved at different temperatures. At lower temperatures of 250°C and 275°C, the viscosity averaged 5. As the temperature increased to 350°C, there was corresponding increase of viscosity to an average of 6.8. The Engine manufacturers Association's (EMA) recommended that specification for viscosity is between 3.5 – 5.0. Diesel with a low viscosity may not provide sufficient lubrication for the precision fit of fuel injection pumps, resulting in leakage or increased wear. Also, diesel viscosities above 5, tend to form larger droplets on injection which can cause poor combustion, increased exhaust smoke and emissions.

6.3.4.2 Iodine Number

Figure 6.6 below represents the Iodine numbers that were measured from the biodiesel produced when the feedstock used was tall oil fatty acid. These iodine numbers were measured at different temperatures, as indicated below.

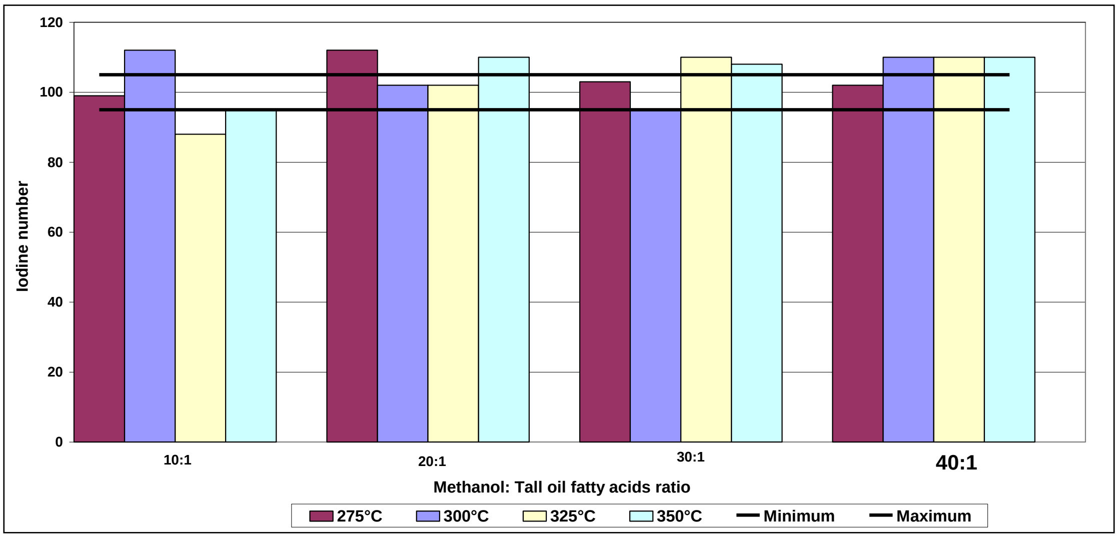


Figure 6.6 – Iodine number (TOFA)

It can be observed on the figure above that there was no correlation between the increase in temperature and the increase in feedstock to methanol ratio that was observed. The recommended Iodine number for a stable biodiesel is between 95 and 105. A higher Iodine number indicates a higher quantity of double bonds in the sample, greater potential to polymerise and, hence, lesser stability.

6.3.4.3 Cetane number

Figure 6.7 below represents the cetane numbers that were measured from the biodiesel produced when the feedstock used was tall oil fatty acid. These cetane numbers were measured at different temperatures, as indicated below.

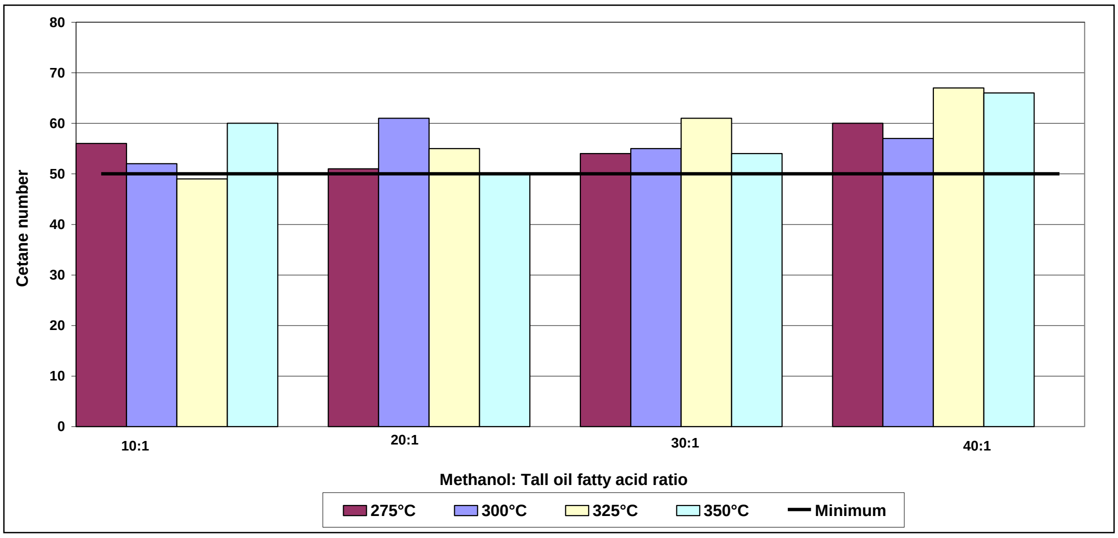


Figure 6.7 – Cetane number (TOFA)

It can be observed from the figure above that almost all diesel produced at different temperatures had a cetane number above 50. A slight increase in cetane number with increasing temperature is observed. At 250°C and 275°C, the average cetane number was 55 and 54 respectively. At higher temperatures of 325°C and 350°C, the cetane number increased to 57 and 58 respectively.

The Engine Manufacturers Association (EMA) recommends a cetane number of 50 for a diesel engine to operate best. The higher the cetane number, the shorter the delay interval and the greater its combustibility. Higher cetane numbers have been associated with a reduced engine roughness and with lower starting temperatures for engines. Good ignition from a recommended cetane number assists with easy starting, starting at low temperature, low ignition pressures, and smooth operation with lower knocking characteristics. Lower than recommended cetane number fuel results in poor ignition qualities causes misfiring, tarnish on pistons, engine deposits, rough operation and higher knocking and thus high noise levels (Midwest Biofuels, 1994).

6.3.4.4 Flash Point

Figure 6.8 below represents the flash points that were measured from the biodiesel produced when the feedstock used was tall oil fatty acid. These flash points were measured at different temperatures, as indicated below.

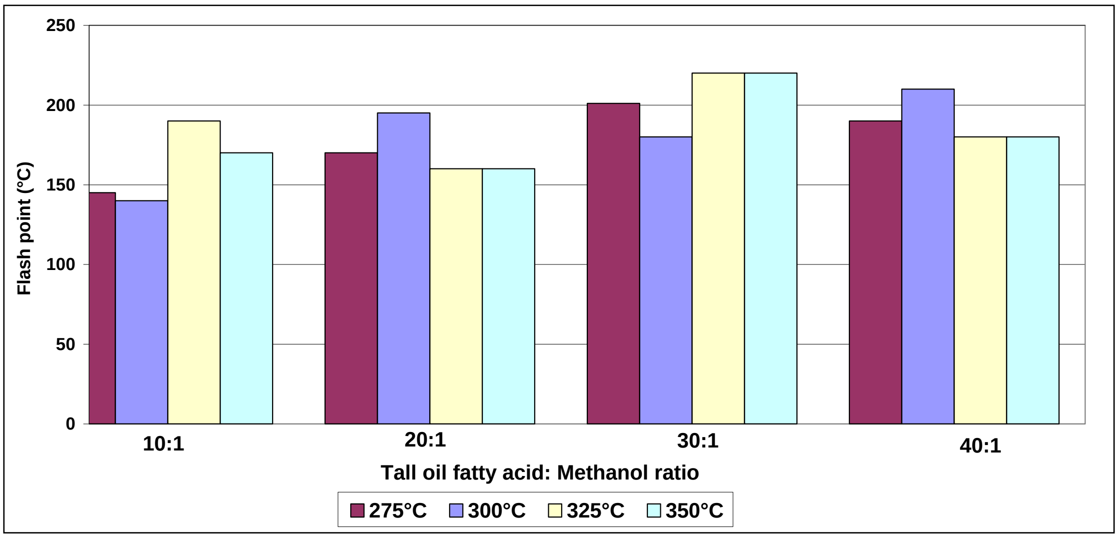


Figure 6.8 – Flash point (TOFA)

It can be observed from the figure above that there was no correlation with regard to the different temperatures and different methanol to feed ratios for the flash point achieved. At temperatures of 250°C and 275°C, the average flash point was 170 and 167 respectively. At higher temperatures of 325°C and 350°C, the average was 170 and 177 respectively. Biodiesel has a flashpoint of over 160°C which means that the fire hazard potential associated with transportation, storage and usage of biodiesel is much lower than with other commonly used fuels (Biodiesel Education, 2006).

6.3.4.5 Density

Figure 6.9 below represents the densities that were measured from the biodiesel produced when the feedstock used was tall oil fatty acid. These densities were measured for different temperatures, as indicated below.

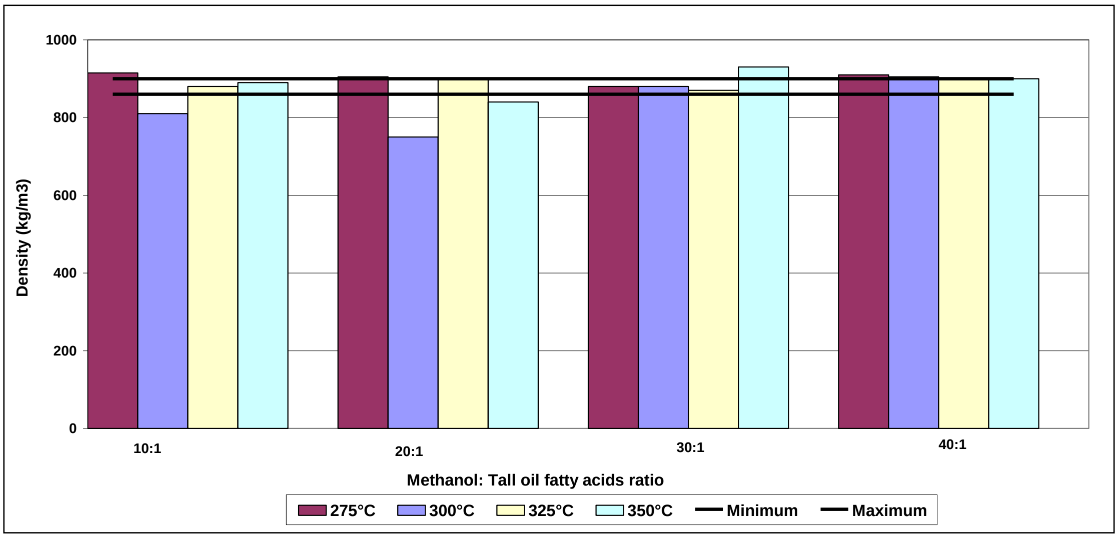


Figure 6.9 – Density (TOFA)

It can be observed from the above figure that there is slight difference (20 kg/m^3) between densities measured for all biodiesel produced at different temperatures. This is indicate by the fact that, at temperatures of 250°C and 275°C, the average density was 920 kg/m^3 and at temperatures of 325°C and 350°C, the average density was 900. This finding indicates that as temperature increases, the density decreases.

This is in line with the studies done by Minami and Saka (2006) on rapeseed oil, where they found that as temperatures reached 300°C, the density would begin to drop. They did not offer an explanation for this phenomenon.

The Engine Manufacturers Association (EMA) recommends a density of 880 kg/m^3. Oils that are denser contain more energy. For example, petrol and diesel fuels give comparable energy by weight, but diesel is denser and hence gives more energy per litre.

6.3.4.6 Acid Value

Figure 6.10 below represents the acid value numbers that were measured from the biodiesel produced when the feedstock used was tall oil fatty acid. These acid values numbers were measured at different temperatures as indicated below.

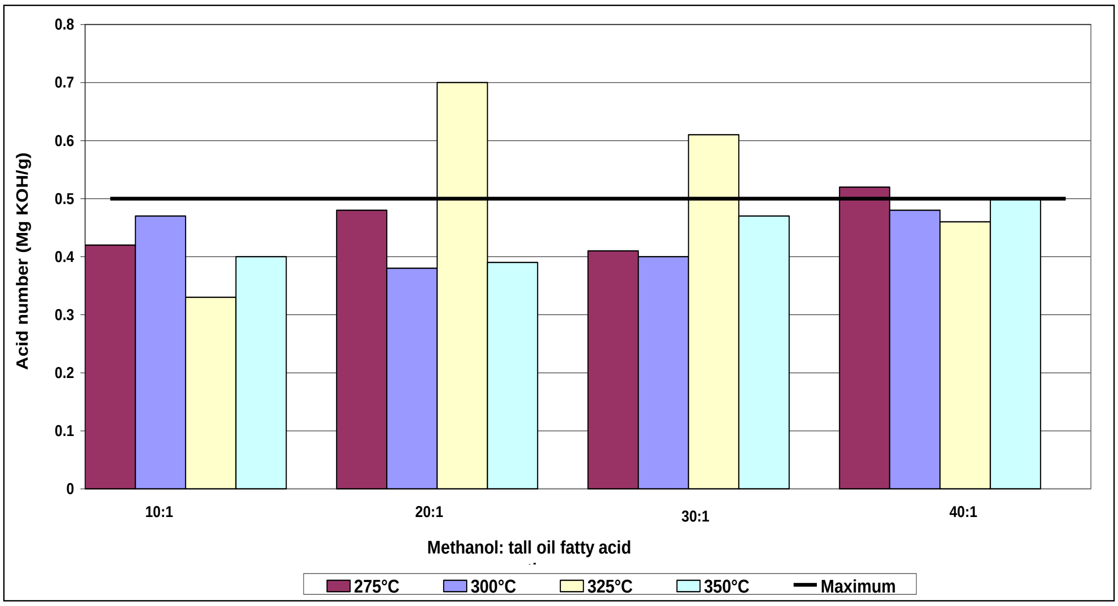


Figure 6.10 – Acid value numbers (TOFA)

It can be observed from the figure above that the Acid Number reflects the fatty acid content in the biodiesel. The effect of esterification is to reduce the level of fatty acids greatly. There appears to be a correlation between the increase in temperature and the acid number. The average acid number for 250°C and 275°C was found to be 0.25 and 0.45 respectively. At higher temperatures of 325°C and 350°C, the acid number was 0.50 and 0.57 respectively.

The ratio of methanol and feedstock also followed a similar trend, that when the ratio was increased, the acid number also increased. However, at higher temperatures this trend was not evident.

6.3.4.7 Melting Point

There was no significant difference in the melting point across the different temperatures and methanol to feedstock ratio. In cases where the temperatures fall below the melt point, the entire fuel system, including all fuel lines and fuel tank, will need to be heated.

6.3.5 Biodiesel Parameters that impact on the Environment

6.3.5.1 Sulphur Percentage

Figure 6.11 below represents the sulphur percentages that were measured from the biodiesel produced when the feedstock used was tall oil fatty acid. These sulphur percentages were measured at different temperatures as indicated below.

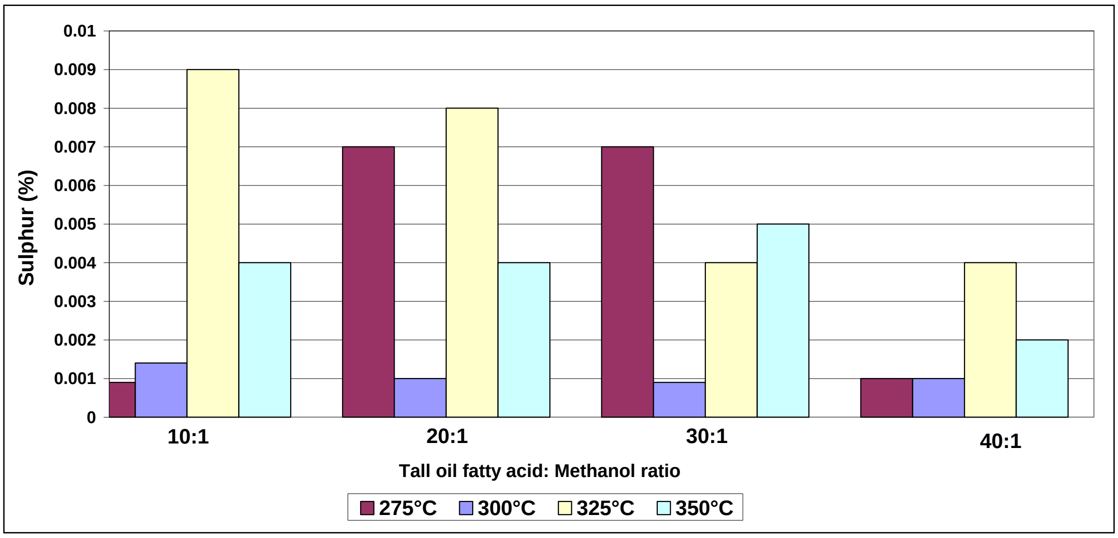


Figure 6.11 – Sulphur percentage (TOFA)

It can be observed from the above figure that there was no correlation between the sulphur percentage across all the different temperatures and methanol to feed stock ratios. Since 1995 the sulphur content of fossil diesel must be below 50 ppm (SAPIA, 2006) because high sulphur contents in fuels have been associated with negative health effects and an increased service frequency on vehicles.

6.3.5.2 Ash percentage

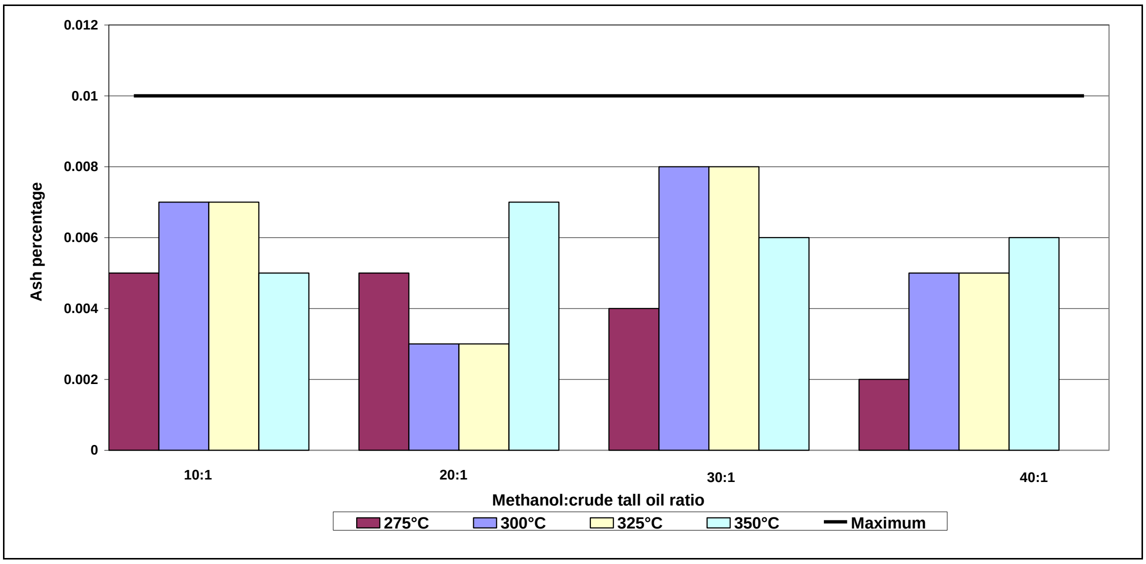


Figure 6.12 – Ash Percentage (TOFA)

There was no correlation in the Ash percentage achieved across the different temperatures and different methanol to feed ratio. However, the Engine Manufacturers Association (EMA) recommends an Ash percentage of below 0.01. All Ash percentages measured for the different temperatures were below 0.01. A high concentration of Ash can cause injector tip plugging, combustion deposits and injection system wear. It is important for heating value, as heating value decreases with increasing ash content.

6.4 Conversion of Crude Tall Oil

6.4.1 Effect of time

The figure below represents the effect of time on biodiesel yield.

The figure below represents the effect of time on biodiesel yield across different temperatures when crude tall oil was used as a feedstock.

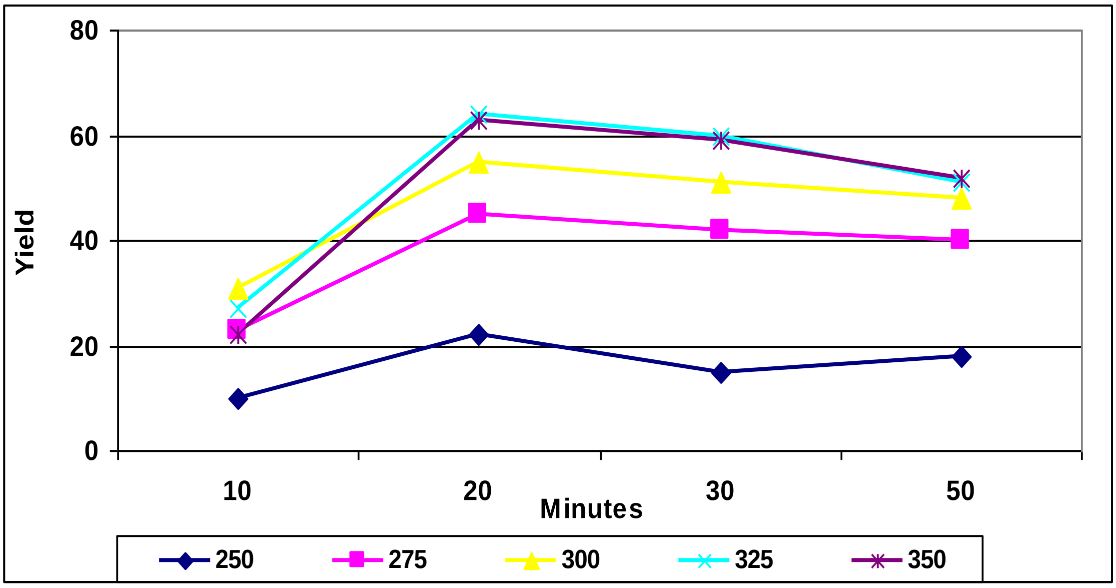


Figure 6.13 – Effect of time on biodiesel yield (10, 20, 30 and 50 minutes)

From the graph above, it can be noted that there was an increase in biodiesel yield as the reaction time increases from 10 to 20 minutes. The yield dropped slightly after 20 minutes and dropped further from 30 to 50 minutes. However, a different trend was observed for a reaction temperature of 275°C. Though the yield dropped after 20 minutes, it picked up slight after 30 minutes from 16% to 19%.

During a **10 minute reaction time**, the biodiesel yield was between 20% and 30% for all the temperatures. When the reaction time increased from 10 minutes to 20 minutes, the biodiesel yield increased to 64% at 325°C. For the experiment samples that were heated up to 275°C and 300°C, there were increases to 44% and 53% respectively at the reaction time of 20 minutes. These yields were the highest that were achieved during the experiments. For the temperature at 350°C, which was the highest temperature for the experiment, the biodiesel yield was 62%.

For the **30 minutes reaction time**, the highest biodiesel yield was 60% and this was achieved at 325°C. The lowest yield was achieved at 18% for the sample that was heated up to 250°C. A yield of 41% and 48% was achieved for the samples that were heated up to temperatures of 275°C and 300°C, respectively.

For the **50 minutes reaction time**, the highest yield of 52% was achieved at 325°C. The lowest yield was achieved at 18% at a temperature of 250°C.

It was observed when the feedstock was tall oil fatty acids, the highest yield across different times and temperatures was achieved at 325°C.

6.4.2 Effect of methanol: crude tall oil ratio

Figure 6.14 indicates the yields of biodiesel over the ratio of methanol and tall oil across different temperatures.

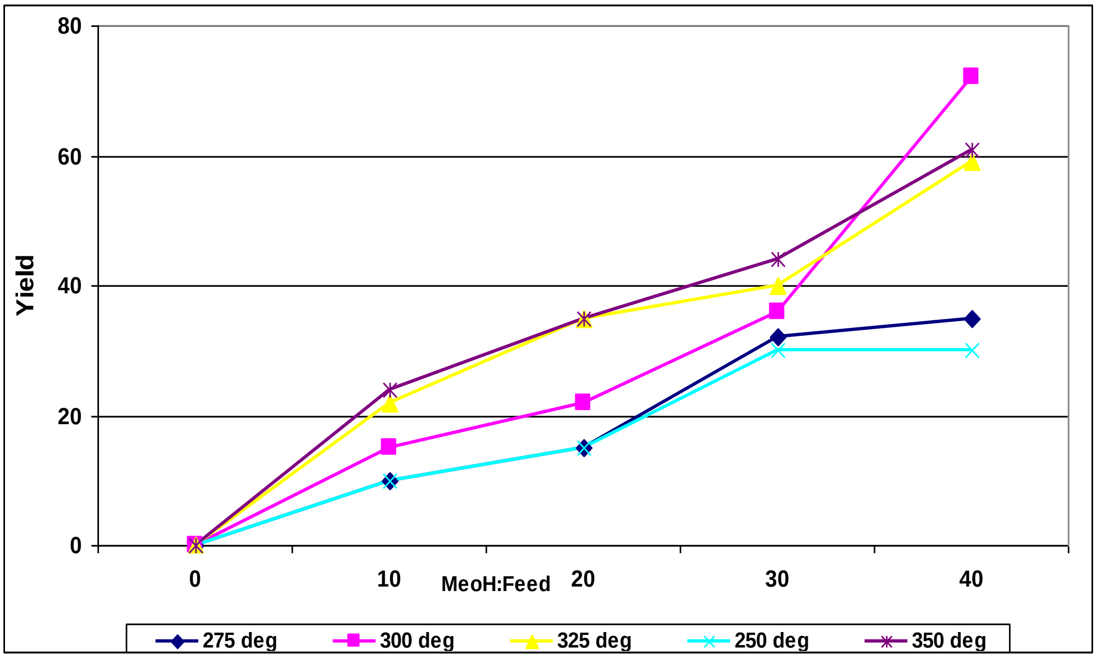


Figure 6.14 – The effect of methanol: oil ratio on biodiesel yield

There is a correlation which is similar to what was observed on Figure 6.14 where the yield increased with the increase in methanol to feed ratio. However, the maximum yield achieved with the tall oil was 69% compared to 83% on tall oil fatty acid.

6.4.3 Effect of temperature on biodiesel yield

The figure below indicates the effect of temperature on biodiesel yield at different methanol to crude tall oil ratios.

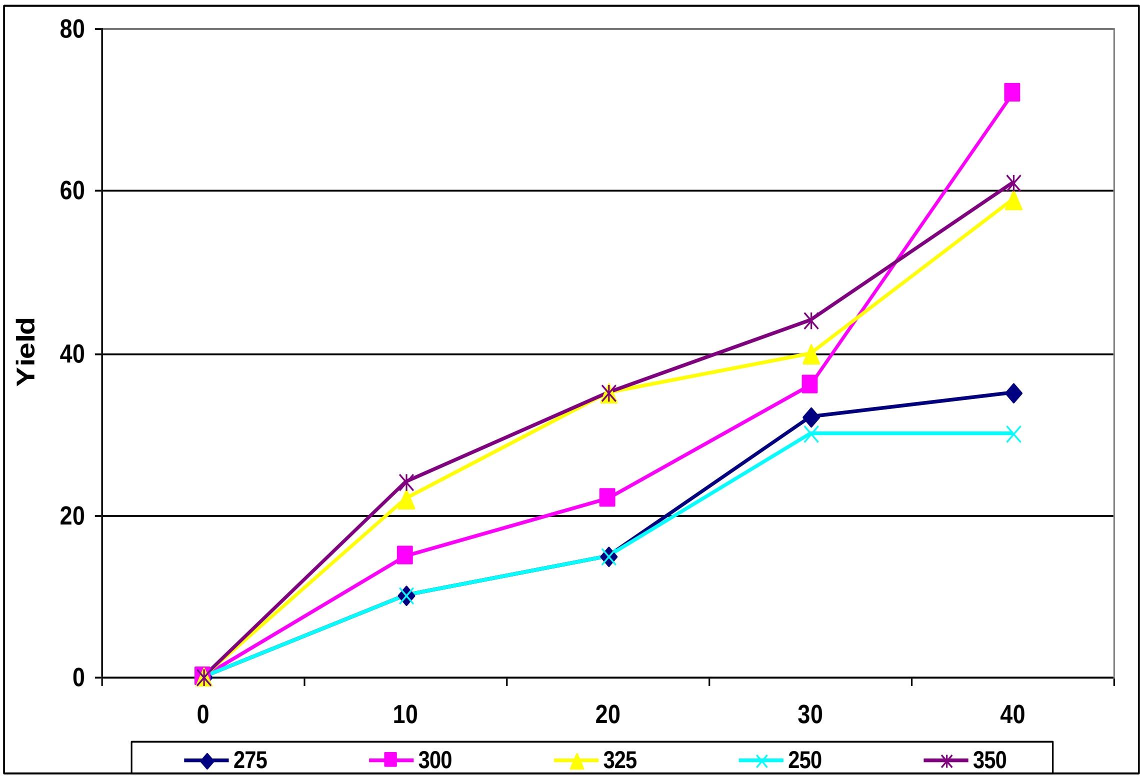


Figure 6.15 – The effect of temperature on yield

There was an increase in biodiesel yield with the increase in temperature. At a temperature of 250°C and a methanol to oil ratio of 40:1, a yield of 30% was observed. A maximum yield of 72% was achieved with the temperature of 300°C at a methanol to oil ratio of 40:1. For a temperature of 350°C, a lower yield of 61% was achieved. A lower yield was expected under those conditions because the crude tall oil contains a portion of resin acids and unsaponifiable which hinder the conversion of oil into biodiesel.

The findings of this study were consistent with the results of the study on tall oil fatty acid reported earlier in this Chapter, where it was observed that an increase in yield was achieved with the increase in temperature.

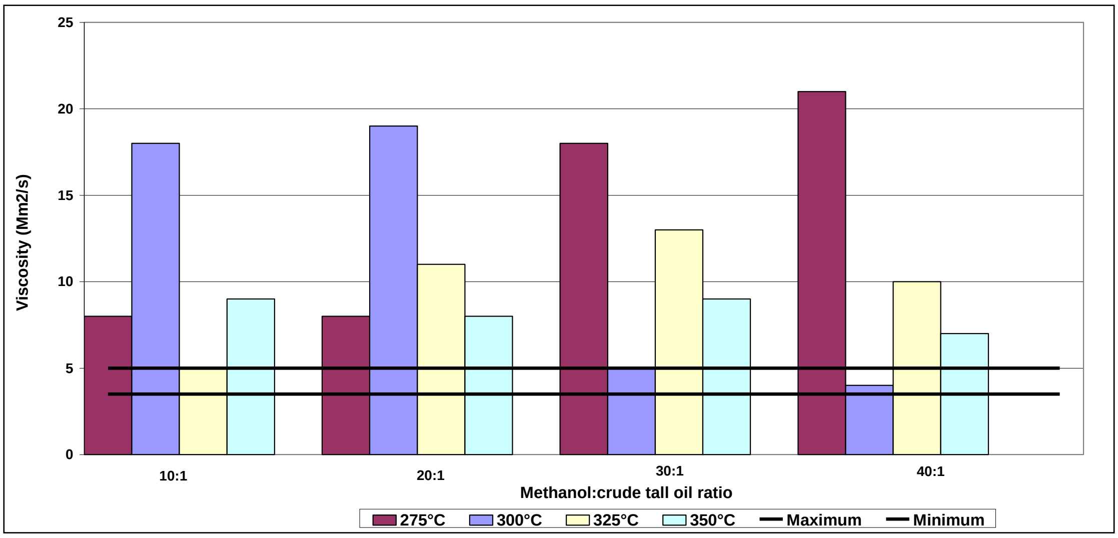
Table 6.4 Biodiesel parameters (275°C and 375°C)

Biodiesel parameters (250 deg)								
Performance indicator								
	275				325			
Feed stock: methanol	10	20	30	40	10	20	30	40
Melting point	-2	-5	-6	-3	-4	-6	-8	-5
Flash point	140	155	160	150	170	210	160	190
Iodine number	103	95	103	100	**107**	102	95	110
Viscosity	**8**	**8.2**	**7.9**	**8.9**	**5.4**	5	5.3	4.1
Cetane number	55	**47**	50	52	50	57	51	55
Density	**820**	**950**	900	**850**	890	900	860	900
Acid value	0.23	0.38	0.36	0.43	0.44	0.47	0.49	0.51
Environmental indicator								
Ash percentage	0.005	0.05	0.004	0.02	0.007	0	0.008	0.005
Sulphur percentage	0.0006	0.0002	0.0003	0.0004	0.0007	0	0.007	0.005
Potassium percentage	2.7	3.3	5.3	6.8	7	5	8	7

The above table indicates the biodiesel parameters that were analysed and reported. Due to the costs of conducting the above tests, the biodiesel parameters were tested for 250°C and 325°C.

6.4.4 PARAMETERS THAT IMPACT ON PERFORMANCE

6.4.4.1 Viscosity

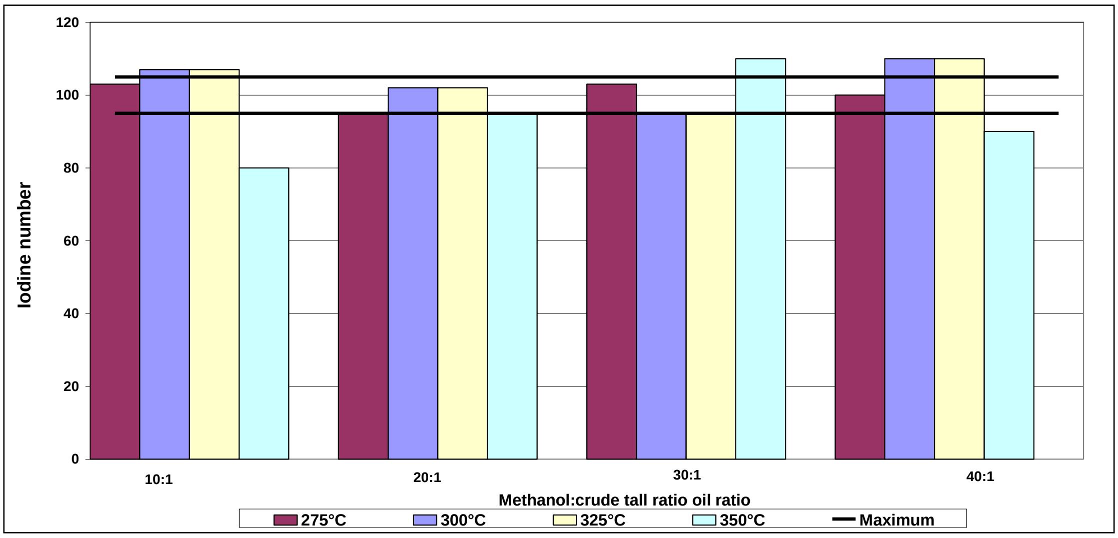


An inverse relationship was observed between the temperature and the viscosity. At the low temperature of 275°C, an average viscosity of 8.3 was observed. At temperature of 325°C, an average viscosity of 5.1 was observed.

This was not consistent with the findings of the study with the tall oil fatty acids Minami and Saka (2006), where there was a correlation with the tall oil fatty acid. In that study, when the tall oil fatty acid temperature increased, the viscosities increased.

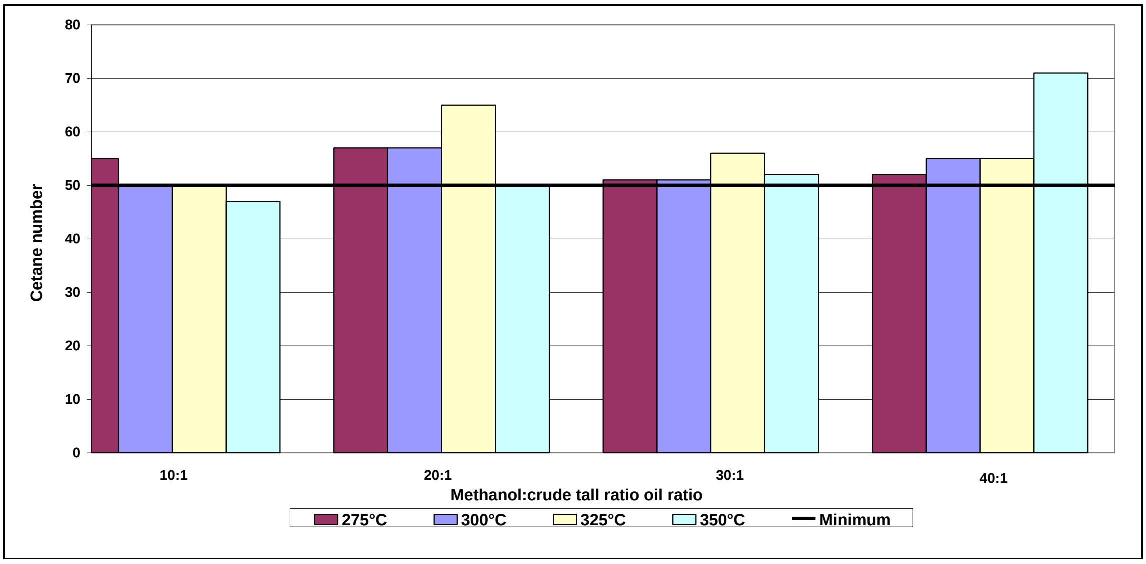
The Engine Manufacturers Association (EMA) recommends that viscosity should be between 1.9 and 4.1. Biodiesel produced from the tall oil does not meet the specification of the EMA. When used in engines, these viscosities will tend to form larger droplets on injection which can cause poor combustion and increased exhaust smoke and emissions because they are above the maximum specification of 5.

6.4.4.2 Iodine Number



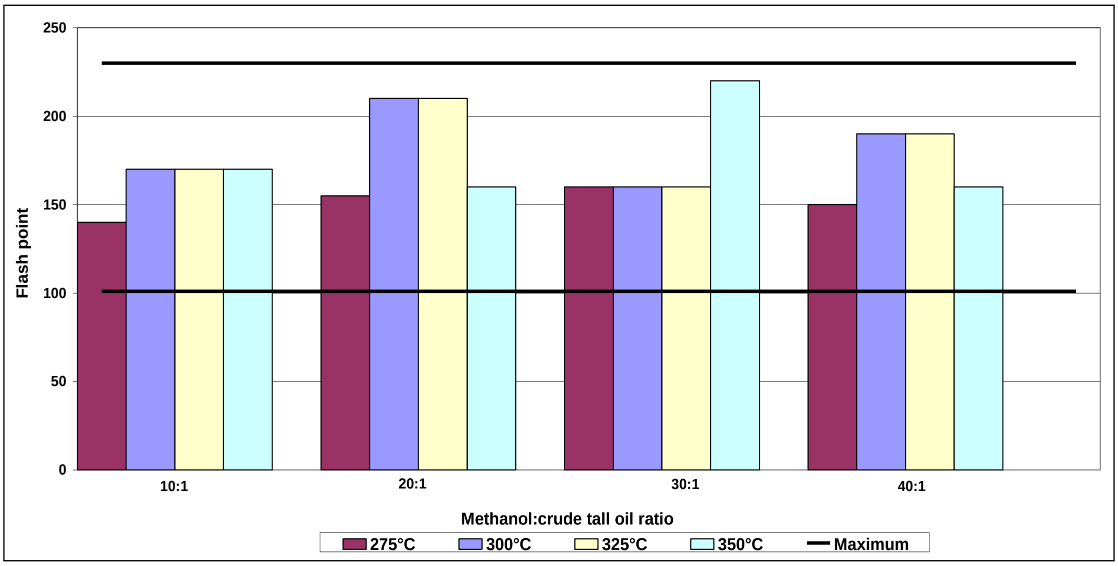
A temperature of 275°C yielded an average iodine number of 103 compared to the temperature of 325°C which yielded an average iodine number of 107. Biodiesel produced at either of the two temperatures will be a stable product. The recommended Iodine number for a stable biodiesel is between 95 and 105.

6.4.4.3 Cetane Number



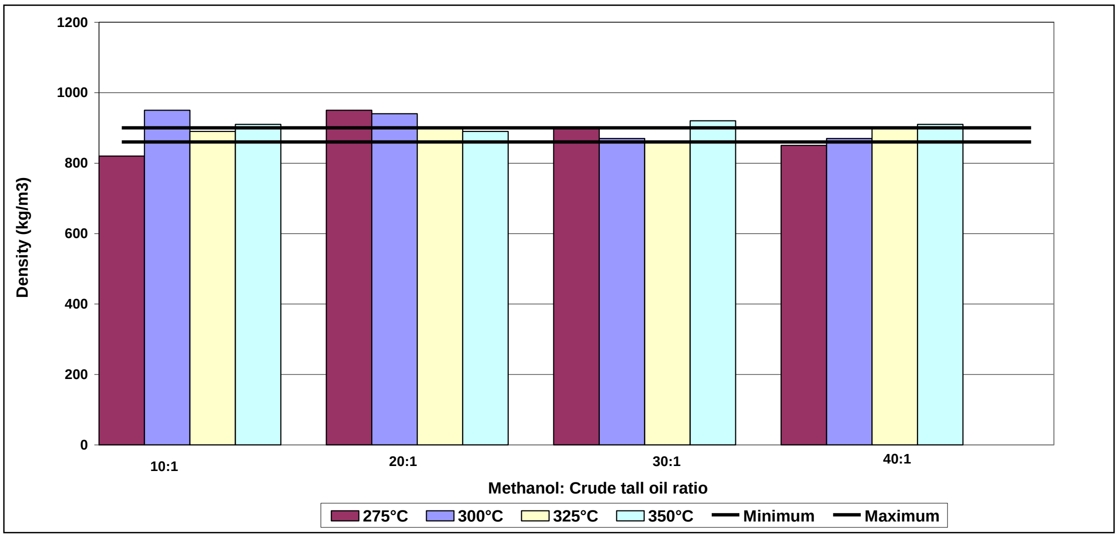
The biodiesel produced at the temperature of 275°C had an average cetane number of 51 and the biodiesel produced at the temperature of 325°C had an average cetane number of 57. Both biodiesels meet the recommendations of the EMA, which recommends a cetane number of 50. This biodiesel produced will not result in difficult starts, noise or exhaust smoke.

6.4.4.4 Flash Point



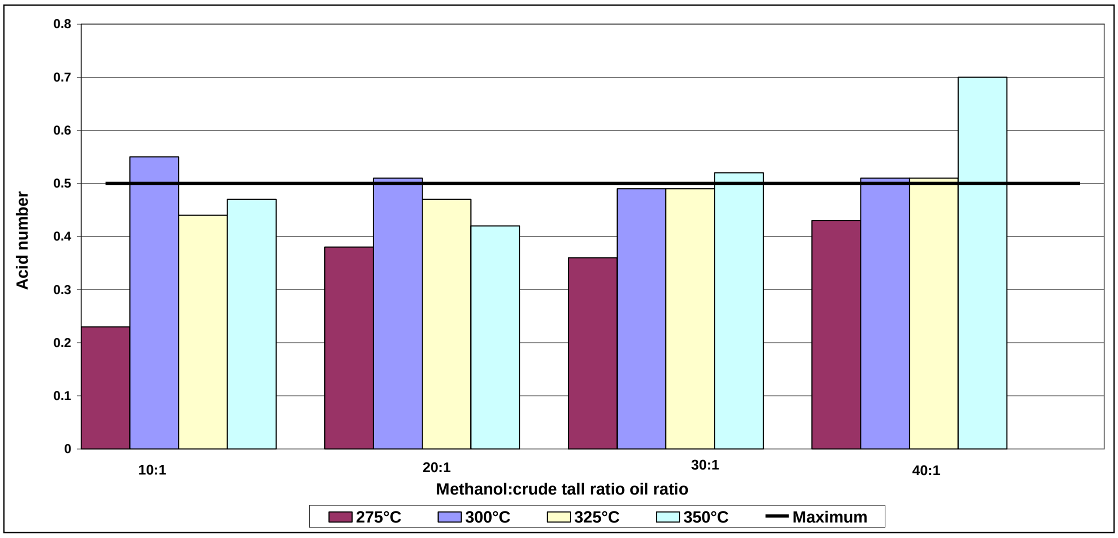
The average flash point for the biodiesel produced from the tall oil that was heated up to 275°C was 155. Biodiesel produced from the tall oil that was heated up to 325°C was 180°C. Both biodiesel products are within the recommended specification for the biodiesel which is 160°C. This means that the fire hazard associated with transportation, storage and usage of biodiesel is much lower than with other commonly used fuels (Biodiesel Education, 2006).

6.4.4.5 Density



The average density for the biodiesel produced at 275°C was 870 kg/m^3 and the average density for the biodiesel produced at 325°C was 880 kg/m^3. The Engine Manufacturers Association (EMA) recommends a density of 880 kg/m^3 and therefore both the biodiesel products meet the recommendation.

6.4.4.6 Acid Value



The average acid number for the biodiesel produced at 275°C was found to be 0.36 and the average acid number for the biodiesel produced at 325°C is 0.48. The increase in temperature from 275°C to 325°C resulted in the increase of 75% in acid number. This is consistent with the resulted achieved with the tall oil fatty acid conversion to biodiesel.

The results suggest that there are more fatty acids in the biodiesel produced at a temperature of 325°C as compared to the biodiesel produced at 275°C. The reaction was more complete at a temperature of 275°C than at an elevated temperature of 325°C.

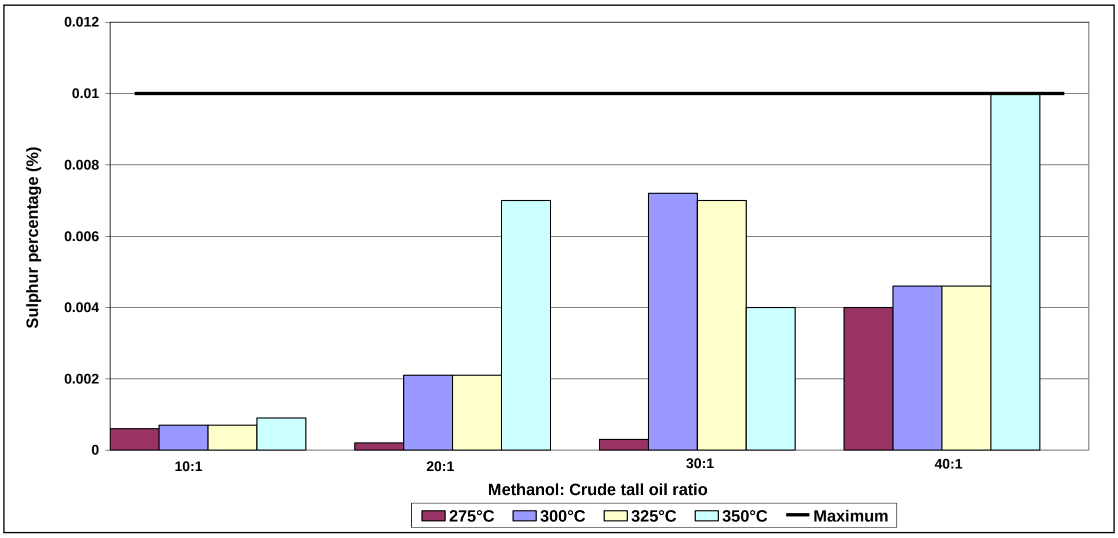
The ratio of methanol and feedstock does not seem to have an effect on acid value.

6.4.4.7 Melting Point

There was no significant difference in the melting point across the different temperatures and methanol to feedstock ratio. In situations where the temperatures fall below the melt point, the entire fuel system, including all fuel lines and fuel tank, will need to be heated.

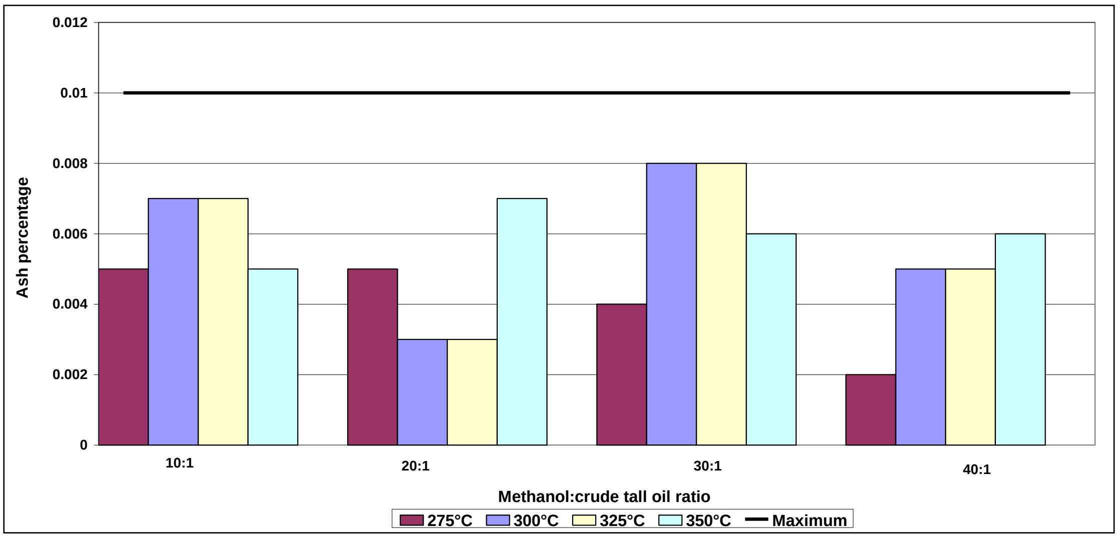
6.4.5 PARAMETERS THAT IMPACT ON ENVIRONMENT

6.4.5.1 Sulphur Percentage



There was no correlation between sulphur percentages across the different temperatures and methanol to feed stock ratios. Since the beginning of 2005, the sulphur content of fossil diesel has to be below 50 ppm (SAPIA, 2006) as high sulphur contents in fuels have been associated with negative health effects and an increased service frequency on vehicles.

6.4.5.2 Ash percentage



There was no correlation in the Ash percentage achieved across the different temperatures and different methanol to feed ratios. However, the Engine Manufacturers Association (EMA) recommends an Ash percentage of below 0.01. All Ash percentages measured for the different temperatures were below 0.01. Higher concentrations of Ash can cause injector tip plugging, combustion deposits and injection system wear. This is an important factor for heating value, as heating value decreases with increasing ash content

6.5 Comparison of TOFA and CTO

Below is a comparison for the biodiesel produced from both the feedstocks. The first part of this section will be a comparison of process parameters, i.e. time, feedstock to oil ratio and temperature.

6.5.1 Process parameters

Tables 6.5 and 6.6 are the tabular representation of the highest biodiesel yield achieved and their corresponding feedstock to methanol ratio, temperature and reaction time for both tall oil fatty acids and crude tall oil.

Table 6.5 Highest biodiesel yield – Tall Oil Fatty Acids (TOFA)

Yield	Ratio	Temperature (C)	Time (min)
83	40:1	325	20

Table 6.6 Highest biodiesel yield – Crude Tall Oil (CTO)

Yield	Ratio	Temperature (C)	Time (min)
69	40:1	350	20

6.5.1.1 Effect of Time

The highest biodiesel yield of 83% was achieved at 20 minutes for the tall oil fatty acids, whereas a maximum yield of 64% was achieved at the same reaction time for the crude tall oil.

6.5.1.2 Effect of feedstock: oil ratio

The highest biodiesel yield of 83% was achieved at 40:1 ratio of methanol to tall oil fatty acids, and the yield of 69% was achieved when crude tall oil was used.

6.5.1.3 Effect of temperature

The highest biodiesel yield of 83% was achieved at 325°C for the tall oil fatty acids, and the highest biodiesel yield of 67% was achieved at 350°C when the feedstock was crude tall oil.

6.5.2 Biodiesel Parameters

6.5.2.1 Iodine numbers

Iodine numbers for both biodiesel products produced from tall oil fatty acids and crude tall oil were between 95 – 105, which is an acceptable range as per the Engine Manufacturers Association.

6.5.2.2 Cetane number

Cetane numbers for the biodiesel products produced from both the feedstock above 50, as per Engine Manufacturers Association.

6.5.2.3 Flash point

Flash points for the biodiesel products produced from both the feedstock were at an acceptable level of above 160.

6.5.2.4 Density

Densities for the biodiesel products that were produced from both tall oil fatty acids and crude tall oil were within 880 kg/m3 which is recommended by Engine Manufacturers Association.

6.5.2.5 Acid value

6.5.3 Environmental Parameters

Sulphur and Ash percentages for both the feedstocks were at an acceptable level of below 0.01.

6.6 Summary

This Chapter presented the results that were achieved from the test work. The two feedstocks, i.e. tall oil fatty acids and crude tall oil were evaluated separately. There were three process parameters that were evaluated to establish if they have any effects on the biodiesel yield produced from the feedstocks, i.e. reaction time, methanol to feedstock ratio and temperature.

The highest yield of 83% was achieved when feedstock used was tall oil fatty acid, the process conditions were 20 minutes reaction time, 40:1 methanol to feedstock ration at 325°C. There was no significant increase after 20 minutes which would justify running a process longer. This would consume excess energy without any significant return on biodiesel yield. The temperatures below and above 325°C didn’t yield a biodiesel yield higher than 83%. The ratio of 40:1 of methanol to feedstock ratio resulted in the highest yield. The presence of higher methanol concentration is believed to have assisted with the conversion rate to biodiesel.

The highest yield of 69% was achieved when the feedstock used was crude tall oil. This yield was achieved at 350°C and 30 minutes. This can be attributed to the fact that CTO contains rosin and pitch and, together, they are not converted to biodiesel with the supercritical methanol treatment process.

The performance and environmental indicators of the biodiesel produced were evaluated. It was concluded that the biodiesel produced from tall oil fatty acid meets the specifications of the Engine Manufacturers Association. However, the biodiesel produced from the crude tall oil did not meet the specification of the Engine Manufacturers Association.

CHAPTER 7

ECONOMIC CONSIDERATIONS

7.1 Introduction

This Chapter details the economic considerations for the production of biodiesel from the two feedstocks used for this study. Firstly, this Chapter will calculate the possible income likely to be generated on the project, based on the maximum yield achieved on each feedstock. Secondly, this chapter will discuss the issues that will affect the overall economics of the project, which will need to be considered. This latter discussion will include the feedstocks as well as operating parameters.

7.2 Possible income

This table below represents the possible income likely to be generated from the two feedstocks. The parameters that were used for the calculations below are those that achieved the maximum yield for both the feedstocks. Table 7.1 indicates the possible income that will be generated from the biodiesel products generated from both the tall oil fatty acids and crude tall oil.

Based on the tests conducted and reported in the previous Chapter, the methanol to feedstock ratio that gave the most biodiesel yield was 40:1. The temperature for the tall oil fatty acids was 325°C, and was 350°C for the Crude tall oil. Also, the time that gave the highest yield was 20 minutes for the TOFA and 20 minutes for the crude tall oil.

Table 7.1 – Possible Income from Biodiesel

Feedstock type	Tall oil fatty acids (TOFA)	Crude tall oil (CTO)
MeoH: feestock ratio	40	40
Temperature (deg C)	325	350
Time (minutes)	20	30
Yield	83	69
Tonnage (tons/month)	356	304
Biodiesel price (R/kg)	8.5	8.5
Monthly income (Rmil/month)	R 3,026	R 2,584
Yearly income (Rmil/annum)	R 36,312	R 31,008

In the previous Chapter, the tall oil fatty acids had the highest yield of 83% compared to the 76% yield of the crude tall oil. The calculations are shown in the Appendix 4 and are based on the following parameters:-

- 400 tons/month of feedstock;
- R8.5/litre of biodiesel;
- 30 days/month; and
- 12 months/annum.

Based on the calculation above, there is a difference of R5.4 mil/annum. This is, however, consistent with the low yield on crude tall oil of 76% compared to tall oil fatty acid of 83%.

7.3 Operating parameters

There are issues that have an influence on the operating parameters that will need to be considered when the Mill takes the final decision on the project. There parameters are listed below:-

a) Temperature

The highest yield was achieved at a temperature of 325°C for both the feedstock. A higher temperature above this point showed no corresponding increase in the yield, and will result in an increase in steam demand at the utilities plant.

However, to achieve and maintain a temperature of 325°C, at the current operation will require a total re-configuration of the utilities plant. These will include:-

- An increased usage of coal and bark; and
- Human capital.

b) Time

The optimal reaction time for both the feedstock was 20 minutes. The reaction time was increased to 50 minutes, but there was no substantial increase in yield. Ensuring that the reactions are conducted for 20 minutes instead of 50 minutes, will increase the plant output which will have a positive impact on the overall economics of the project as more reactions can be conducted.

c) MeOH

An optimum methanol to feedstock ratio was found to be 40:1 for this study. Any increase in this ratio showed no significant increase in the yield of the final product. Methanol is an expensive commodity and, therefore, has a significant impact on the overall economics of the project.

7.4 Effect of feedstock on economics

This section details the financial impact relating to the two feedstocks that were utilised for the project. These specific issues were discovered during the laboratory evaluations, and will have a significant role in the economic evaluations.

CTO

- This feedstock will require no pre-treatment, and will, therefore, be used in its pure state from the process.
- The additional requirement will be for storing the feedstock prior to pumping into the reactor
- However, the maximum yield that was achieved for this feedstock was 64%. This indicates that there is about 36% of the unsaponifiable material that was left with the final product. Therefore, product separation will be required after the conversion process.
- Though there is no pre-treatment required, there is a post-treatment requirement with this feedstock which will also require capital investment which in turn impact the income generated by this project.

TOFA

- Though the yield is higher than that of crude tall oil feedstock, it should be noted that the product will have to undergo further processing prior to converting it into biodiesel. This will require a huge capital investment and sophisticated equipment including a distillation column.
- However, there will be additional income that will be generated from the commercialisation of the remaining components after distillation i.e. rosin and pitch.

7.5 Summary

This Chapter focused on the economic consideration for the project. Based on the biodiesel yields that were produced, it was established that the revenue likely to be generated by converting crude tall oil into biodiesel was less compared to the revenue generated from tall oil fatty acids. This difference in yield was attributed to the presence of rosin and pitch in the crude tall oil, as they are not convertible into biodiesel by supercritical methanol treatment.

The influences on operating parameters and the feedstocks on the overall economics of the project were also evaluated and reported in this Chapter.

CHAPTER 8

CONCLUSION

The objective of this study was to investigate the feasibility of converting crude tall oil and tall oil fatty acids into biodiesel. The global economic recession that took place between 2007 – 2010, had a profound negative impact on the operation and the profitability within the pulp and paper industry. Sappi Tugela reviewed its papermaking process with the view of establishing if they could be ways of generating extra income within the process. It was therefore decided that Crude tall oil that is currently being sold to the third party should be evaluated for biodiesel production.

Crude tall oil and tall oil fatty acids were the two feedstocks that were used during the study. Crude tall oil is a by-product of a paper making process and tall oil fatty acid is a larger component of crude tall oil that requires fractionation distillation to separate from crude tall oil. The latter was therefore purchased from the third party.

A number of possible conversion procedures were considered for this study to ascertain if they can be utilized to convert the two feedstocks into biodiesel. These procedures were base catalysed transesterification, acid-catalysed esterification; enzyme catalysed reaction as well as supercritical methanol treatment.

A criteria was then developed to select the best possible procedure and it was based on the following categories:-

- Reaction conditions;
- Reaction time;
- Ability to convert free fatty acid into alkyl ester;
- Final product yield;
- Complexity of the process;
- Catalyst requirement; and
- Pre-treatment requirement.

Based on the criteria above, supercritical methanol treatment method was selected for the experiment because of mostly the high free fatty acid content within the two feedstocks investigated and the favourable process conditions (temperature and pressure, no pre-treatment required for the feedstock).

An apparatus which consisted of a 2-litre batch reactor was then set-up to perform the supercritical methanol treatment conversion procedure. As indicated earlier, the crude tall oil was sourced from Sappi Tugela and tall oil fatty acid was purchased from Protea Chemicals.

The testing conditions and the range for the study were determined and the effects of the following were investigated:

- Reaction time;
- Reaction temperature; and
- Methanol to feedstock ratio.

A maximum yield of 83% for the biodiesel was achieved when the feedstock investigated was tall oil fatty acid and the yield of 79% was achieved when the feedstock investigated was crude tall oil. A reaction time of 20 minutes, reaction temperature of 325°C and the methanol to feedstock ratio of 40:1 were the optimum process conditions for the maximum yields for both the feedstocks.

It was observed that for both feedstocks that increasing the reaction time didn’t have any significant increase into the biodiesel yield. This observation suggested that it was unlikely that there was any conversion at this transitory heat-up period.

It was also observed that for most of the corresponding temperatures measured for both the feedstock, the yield was always higher on the tall oil fatty acids. This difference in yield can be best explained by the fact that crude tall oil is an unrefined and treated feedstock which was obtained directly from the process as a by-product. It therefore contains rosin and pitch components which constitute about 30 - 35% of total volume. These components are not convertible to biodiesel with the supercritical methanol treatment.

It was also observed that at an equal amount of methanol to feedstock ratio, the yield was also lower on crude tall oil compared to tall oil fatty acids. This low yield will play a significant role when storage of the material, energy required for heating and recovering of the re-usable reactants are being considered.

Properties of the final biodiesel products from both the feedstocks were tested to ascertain if they meet the requirements for the Engine Manufacturers Association. These properties were differentiated as performance and environmental indicators. Performance indicators were the viscosity, iodine and cetane numbers, density of the biodiesel, and the environmental indicators were ash, sulphur and potassium percentages in the final biodiesel products.

Performance indicators for the tall oil fatty acids met the requirements for the Engine Manufacturers Association whereas crude tall oil's performance indicators didn't meet the specification. The environmental indicators for both the final biodiesel products met the Engine Manufacturers Association specification.

An economic consideration to determine the possible income that is likely to be generated from both the biodiesel products was performed. It was established that a yearly income of R 36 million could be realised when the feedstock used is tall oil fatty acids and R 31 million if the feedstock is crude tall oil.

Also, the critical issues that will influence the overall economics of the project when the project is taken to a plant scale were discussed. Though, the preliminary calculations indicate that there is more revenue to be generated if the feedstock used if tall oil fatty acid, but the reality of the matter is that tall oil fatty acids will have to undergo further treatment prior to converting into biodiesel. The costs of pre-treating tall oil fatty acid were not undertaken as it did not form the scope of this project.

The following were the recommendations that emanated from the study:-

- Should there be a need to conduct further trials in a lab scale, it is recommended that a minimum 5 litres of reactor be considered. There was greater difficulty in getting unreacted product after each test, as there were not sufficient materials left in the reactor for sampling

- Due to the difficulties that were experienced in modelling the system and predict the behaviour, an equilibrium data of vapour/liquid/liquid should be obtained to determine binary interaction parameters between each components as well as individual activity co-efficient. Such data would be invaluable for the prediction of the formation of a single fluid phase, saving the researcher from the trial and error exercise.

- The government has a role to play in ensuring that the biodiesel business becomes a success. The policies that the government creates will need to be focused on ensuring that there are incentives for companies that want to produce biodiesel. The researcher did not consider these incentives for this study, but they are bound to play a significant role and they will be largely a part as this initiative progresses. These incentives includes among other things:-

    - Tax incentives;
    - Price compensation agreement;
    - Carbon credit systems;
    - Import tariffs on biofuels; and
    - Rebate on the customs duty on imported feedstock.

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