BIOPETROL SYNTHESIZED FROM RUBBER SEED OIL BY ZEOLITES CATALYST : EFFECT OF OPERATING TEMPERATURE IN CRACKING PROCESS

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SUPERVISOR'S DECLARATION

I hereby declare that I have checked this thesis and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

Signature:

Name of Supervisor: Mr. Syaiful Nizam Bin Hassan

Position: Lecturer

Date: 26 January 2012

STUDENT’S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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ABSTRACT

Petroleum is a fossil fuel which takes millions of years to form. The fossil fuel that used today depleting much faster without suspected. The alternatives fuel must be searched to solve this problems. The rubber seed oil is found to be a promising alternative fuel source to replace petrol fuel. Biopetrol is derived from vegetable oil and also renewable energy source. The objectives of this research are to synthesize biopetrol from rubber seed oil in order to overcome fuel supply problem and to identify the effect of temperature in cracking process using zeolites catalyst for the rubber seed oil production. Soxhlet extractor is used to extract the rubber seed oil from the rubber seed. Then, the hexane is removed by using rotary evaporator to get pure rubber seed oil. The catalytic cracking with presence zeolites as the catalyst is applied to crack the fatty acid complex into smaller hydrocarbon molecules. Five grams of zeolites catalyst is added into the crucible that contain 25 ml rubber seed oil. The mixture is heated in the furnace at 300°C for 15 minutes. After that, the different temperature is used which is 350°C and 400°C in order to see the effect of temperature on the isooctane production. By using the gas chromatography, the presence of isooctane in the sample can be detected which is indicate that biopetrol is produced. Based on this research, the highest amount of isooctane is produced which is 75.3234% at temperature of 350ºC. The presence of temperature and catalyst that used will give the sudden effect to production of isooctane from the rubber seed oil. In conclusion, biopetrol can be produced from the rubber seed oil by zeolites catalyst.

ABSTRAK

Petroleum adalah bahan api fosil yang mengambil masa berjuta-juta tahun untuk terbentuk. Bahan api fosil yang digunakan hari ini semakin berkurangan dengan lebih cepat tanpa disedari. Bahan api alternatif perlu dicari untuk menyelesaikan masalah ini. Minyak biji getah (RSO) didapati menjadi sumber bahan api alternatif yang menjanjikan untuk menggantikan bahan api petrol. Biopetrol berasal daripada minyak sayur-sayuran dan juga sumber tenaga yang boleh diperbaharui. Objektif penyelidikan ini adalah untuk mensintesis biopetrol daripada RSO untuk mengatasi masalah bekalan bahan api dan untuk mengenal pasti kesan suhu dalam proses retak dengan menggunakan pemangkin zeolite untuk pengeluaran minyak biji getah. Alat soxhlet ekstrak digunakan untuk mengekstrak RSO dari bijinya. Kemudian, heksana dikeluarkan dengan menggunakan penyejat putar untuk mendapatkan RSO tulen. Proses retak dengan kehadiran zeolite sebagai pemangkin digunakan untuk memecahkan asid lemak kompleks kepada molekul hidrokarbon yang lebih kecil. Lima gram pemangkin zeolite dituang ke dalam mangkuk pijar yang mengandungi 25 ml RSO. Campuran dipanaskan di dalam ketuhar pada suhu 300ºC selama 15 minit. Selepas itu, suhu yang berbeza iaitu 350ºC dan 400ºC digunakan untuk melihat kesan suhu ke atas pengeluaran isooktana. Dengan menggunakan alat gas kromatografi, kehadiran isooktana dalam sampel boleh dikesan yang menunjukkan juga bahawa biopetrol dihasilkan. Berdasarkan kajian ini, jumlah tertinggi isooktana adalah 75.3234% iaitu pada suhu 350ºC. Kehadiran suhu dan pemangkin yang digunakan telah memberi kesan kepada pengeluaran isooktana daripada RSO. Kesimpulannya, biopetrol boleh dihasilkan daripada RSO dengan menggunakan pemangkin zeolite.

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LIST OF SYMBOLS

O_2	Oxygen
CO_2	Carbon Dioxide
H_2	Hydrogen
N_2	Nitrogen
°F	Fahrenheit
%	Percentage
°C	Celsius
g	gram
ml	millilitre
µl	microlitre
m	meter
mm	millimetre
min	minutes
pA*s	peak area
kPa	kilo paschal

LIST OF ABBREVIATIONS

CI	Compression ignition
GRG	General rubber goods
HCCI	Homogeneous charge compression ignition
PRF	Primary reference fuel
SI	Spark ignition
RSO	Rubber seed oil
LPG	Liquefied petroleum gas
GC	Gas chromatography
GLC	Gas liquid chromatography
GSC	Gas solid chromatography
WCOT	Wall-coated open tubular
SCOT	Support-coated open tubular
CEC	Cation exchange capacity
GCMS	Gas chromatography mass spectrometry

CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACKGROUND

Petrol or gasoline is a complex mixture of over 500 hydrocarbons that may have between 5 to 12 carbons. It is produced by mixing fractions obtained from the distillation of crude oil (petrochemicals) with brand-specific additives to improve performance. It is a volatile liquid with a characteristic odour under normal conditions. In this century, petrol is the most demanding fuel. Usually, petrol is mainly used as a fuel for road vehicles such as cars, motorbikes and vans. In smaller engines (two stroke), petrol is mixed with oil to produce a fuel mixture that can reduces engine wear. However, petrol is non-renewable energy.

The solution of petrol demand is biofuel. Biofuel can be defined as combustible plant or animal material that can be used as an energy source. The simplest example of biofuel is wood. Wood-burning as a heat and light source has been popular for millennia. Biofuels are also made from sugar cane, soybean algae, vegetable oil and others. The environmental pollution and diminishing supply of the fossil fuels in today are the main factor leading to search for finding the alternative source of energy. When the petrol or diesel are burnt, the carbon atoms will react with O_2 at atmosphere to form Carbon Dioxide (CO_2). This situation can contribute to global warming and also greenhouse effect. Biofuel or bioorganic fuel is considered to be more environmentally responsible type of fuel compared to original oil and fossil fuel product. They have many advantages in terms of ecological sustainability.

Biopetrol or the alternative for petrol is derived from vegetable oil and it is renewable energy sources. The characteristics of biopetrol are it is no sulphur content, non toxic, offer no storage difficulty and excellent lubrication properties. It is proven by many research has been done before. Many developing and industrialized country such as Japan have expressed interest to this relevant idea.

The rubber seed oil, a non-edible type of vegetable oil has been considered as a potential alternative fuel for compression ignition (ci) engines. It has contain many fatty acid in order to produce biopetrol. In this research, catalytic cracking with presence of zeolites catalyst is applied to break the fatty acid in the rubber seed oil to get the isooctane.

1.2 PROBLEM STATEMENT

Petroleum is formed from the remains of tiny sea plants and animals that died millions of years ago. It is a non renewable energy source. This petroleum source cannot be depended at all because petroleum will be exhausted. Oil is the limited resource and has high demands every time. In the middle of 2008, the oil price increase dramatically as shown in Figure 1.1 and Figure 1.2. The instability of the oil world, give the bad response to the peoples in the world. It is because everything to be more expensive caused by the increasing price of petrol. Thus, the alternative source for petroleum is important in overcome this problem. The alternative source like biopetrol is the answer for this polemic because it is cheaper and safer than fossil fuel.

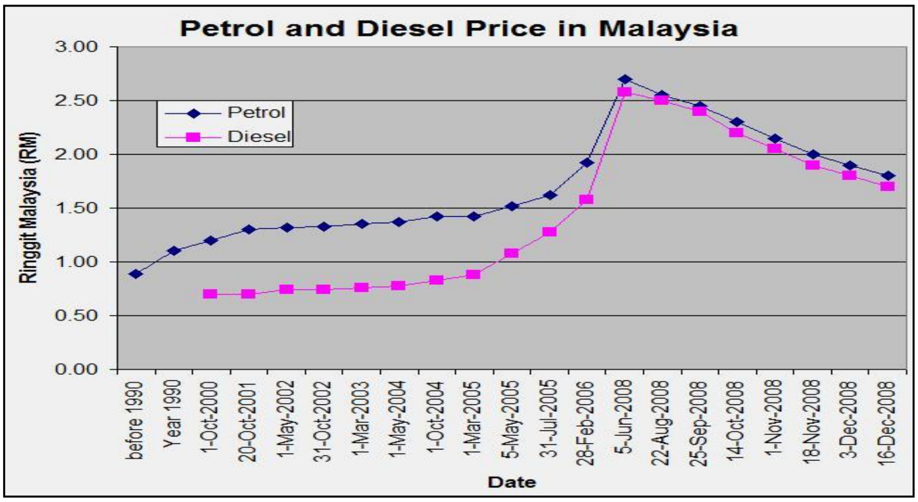

Figure 1.1 : Complete Malaysia Petrol and Diesel Price Chart Since 1990 (updated 0n Jan 09)

Source: OPEC (2008)

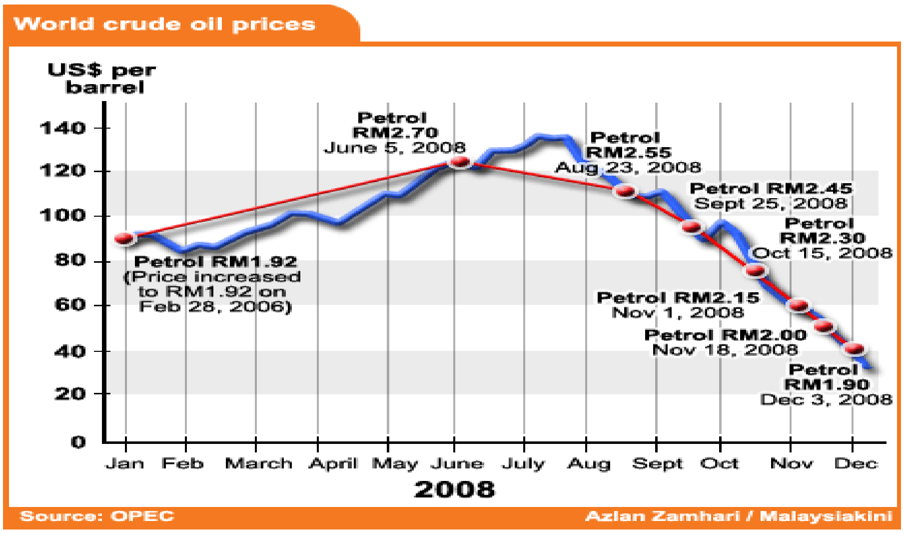

Figure 1.2 : World Crude Oil Prices

Source: OPEC (2008)

Petroleum fuels which is used for power vehicles, household heat generation, generate electric power are the main causes of air pollution. The use of petroleum every day can give the bad effect to environment. When the petroleum is burning, it will generates gases such as carbon monoxide, nitrogen oxides and sulphur dioxides. Sulphur dioxide and nitrogen oxides can react with water in the atmosphere. This situation can increase the acidity of water. Then, the water fall back to the surface earth and damaging property and pollute the environment. This phenomenon is called acid rain.

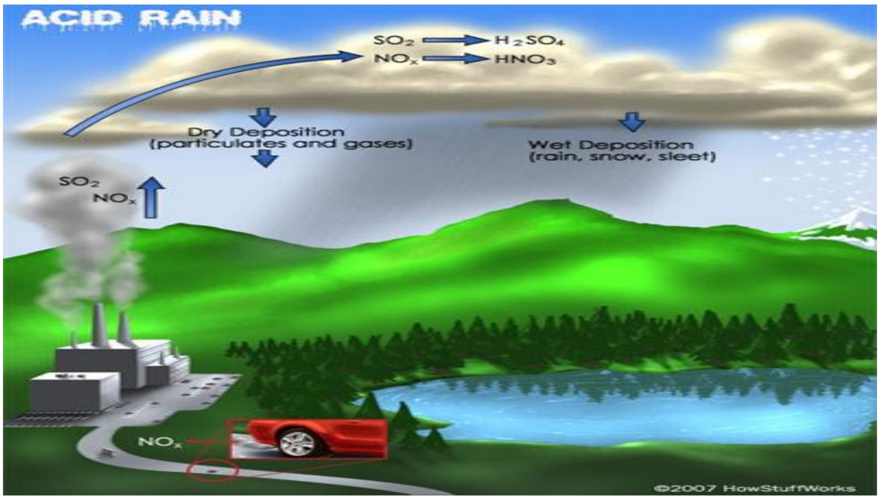

Figure 1.3 : Acid Rain Production

Source : Ramadhas A.S. et al. (2005)

Besides, some of scientist believes that petroleum use is the cause in global climate change. As a result, the average temperature of Earth's surface increases from 0.7 to 1.4°F since the late 1800's. The raising concentrations of green house gases also are responsible for some or all this warming. Carbon dioxide and methane are the gas from greenhouse will trap heat from the sun and hold it near Earth's surface. After the beginning of Industrial Revolution from the late 1700's to the mid-1800's, the concentration of carbon dioxide increase by 30 percent. On the that time, large amounts of petroleum and coal are used by people as power-driven machinery largely replaced hand labour. Some scientist who believes human activities contribute to global warming are concerned that warming in the earth will continue and accelerate if fossil fuel consumption continues to grow.

Malaysia is the third largest rubber producer in the world. In 1980, Malaysia has 2.0 million hectare of rubber plantation, however it declined to 1.2 million hectare in 2007. Although, the supply rubber wood declining, value added rubber wood products still continues to be a major export. The use of rubber is widespread, ranging from industrial product and household, entering the production stream at the intermediate stage or as final products. Usually, tire and tube are the largest consumers of rubber. For remaining which is 44% are taken up by the general rubber goods (GRG) sector, which includes all products except tires and tubes. Even the rubber seeds from the rubber plant are not utilized like latex. Actually, rubber seed have many fatty acids which can produce oil. Rubber seed oil can be used in biopetrol production. Biopetrol from the rubber seed oil is comparable with petrol in the market. Even, it has many advantages than petrol. Rubber seed use should be explored and commercialized because it can prevent fuel problem in the future.

Figure 1.4 : Rubber Seed

Source: Ramadhas A. S. et al. (2005)

Fossil fuel take millions years to produce. It was formed from dead plants and animals. The fossil fuel that used today depleting much faster without suspected. Many industries use large amount of fossil fuels to power their machines. The industries which are contributed to the depletion of fossil fuels are the automotive industries, metal industries and also transportation. Besides, individual citizens also to be the factor of depletion of fossil fuel where they the use of electricity and driving cars as example everyday.

The challenge of synthesizing biogasoline from vegetable oils, for example rubber seed oil in this research is the competition of bioalcohols (biomethanol and bioethanol), hydrogen and water those also synthesized for gasoline-used vehicles. Bioalcohols are currently used by several types of latest generation vehicles as alternative of gasoline, however only low portions of bioalcohols are applicable in their mixtures with gasoline, for example 5%, 10% and 25% bioalcohols in E05, E10 and E25 blends without any modifications of gasoline-used engine. This is because bioalcohols are miscible and soluble with water those give negative effect to the engine itself, especially rust and corrosion, even their octane numbers are higher (112 for bioethanol and 106 for biomethanol). Those negative effects possibly occur when the high concentrations of bioalcohols are applied, for example 85% bioalcohol in E85 blend. In order to prevent the negative effect occurrences, the engine should be modified.

1.3 RESEARCH OBJECTIVES

i. To synthesize biopetrol from rubber seed oil in order to overcome fuel supply problem.

ii. To identify the effect of temperature in cracking process using zeolites catalyst for the rubber seed oil production.

1.4 SCOPES OF RESEARCH

In order to achieve the research objectives, the scopes have been identified. There are some scopes that must to be focus in this research:

i. The extraction of rubber seed oil from rubber seeds using Soxhlet Extraction.

ii. The cracking process to crack the fatty acid complex into smaller hydrocarbon molecules.

iii. Using the gas chromatography method to determine the concentration of Isooctane.

1.5 RATIONALE AND SIGNIFICANCE

i. Biopetrol is a renewable energy source and is biodegradable.

ii. Biopetrol helps to reduce pollution and prevent the greenhouse effect

iii. Fatty acid can be found easily in most vegetable oil especially in rubber seed oil

iv. Rubber seeds are easy to be found in Malaysia.

CHAPTER 2

LITERATURE REVIEW

2.1 PETROLEUM

Petroleum is a fossil fuel. It was formed from remains of animals and tiny sea plants that died millions of years ago. The animals and plants which were died would sink to the bottom of the oceans. Then, they were buried by thousands of feet of sediment and sand that turned into rock. Over time, this organic mixture was subjected to enormous pressure and heat as the layers are increased. The mixture changed chemically, breaking down into compounds made of hydrogen and carbons atoms. This formation can only take place within certain geological conditions. Only 2 % of the organic material is transformed into oil under this condition. The crude oil is pumped out of the ground in a black thick liquid solution is also known as petroleum. Petroleum is non-renewable energy source. It cannot form in the short time. Continued and increasing use of petroleum will intensify local air pollution and magnify the global warming problems caused by CO_2 (Shay, 1993).

2.2 ISOOCTANE

Isooctane or the other name 2,2,4-Trimethylpentane is an octane isomer which defines the 100 point on the octane rating scale. In gasoline, isooctane is the important component for it. Usually, the production of isooctane in the petroleum industries is in the big scale because the many application of it in this century. In the alkylation’s process, isobutane react with isobutylene by using a strong acid catalyst. Isobutylene is demerized into isooctane and after that, it is hydrogenated to isooctane in the nexoctane. The best properties of isooctane is it has low toxicity, high colour stability, lack of colour, low odour and rapid evaporation which makes it an excellent solvent for a variety of surface applications.

There are a lot of interest using isooctane as a fuel in investigations of homogeneous charge compression ignition engine (HCCI) in which isooctane is used both as a neat fuel and also as a component in a primary reference fuel blend. Isooctane can improve the efficiency and also performance of currently operating combustors. Besides, it can reduce the production of pollutant species emissions generated in the combustion process. Isooctane is a primary reference fuel (PRF) for octane rating in spark-ignition engine, and when used in compression ignition engine, has a cetane number of approximately 15 (Curran H.J. et al., 2002)

Table 2.1 : Properties of Isooctane

Physical & Chemical Properties	
1. IUPAC Name	Isobutyltrimethylpentane, 2,2,4-Trimethylpentane
2. Appearance	Colourless liquid
3. Molecular formula	C_8H_{18} or $CH_3C(CH_3)_2CH_2CH(CH_3)CH_3$
4. Molecular weight	114.22 g/mol
5. Melting point ^{0}C	-107.38 °C
6. Boiling point ^{0}C	99.3 °C
7. Density	0.688 g/ml, liquid
8. Specific gravity	0.692

Source: Safety (MSDS) for 2,2,4-trimethylpentane

2.3 RUBBER SEED OIL

The rubber plant is a natural source of rubber that has been reported to have oil rich seeds. There are variations in the oil content of the seed for different countries, the average oil yield have been reported to be 40 %. The oil has found little or no economic importance except for scanty reports on its possible uses in soap, alkyd resin and lubricating oil industries. The vegetable oil has the industrial value that depends on its specified fatty acids and the ease with which it can be combined or modified with other chemicals. The percentage of saturated fatty acids (myristic, palmitic, stearic, arachidic, and behenic) in rubber seed oil is 17 – 20 % and the composition of unsaturated fatty acids (palmitoleic, oleic, linoleic, linolenic and arachidolic) is 77 – 82 % (Njoku et al., 1996).

Rubber seed oil (RSO) produces the same power output like diesel but with reduced thermal efficiency and increased smoke emission because of the high viscosity of RSO, which leads to sluggish combustion (Edwin Geo V. et al., 2009). The rubber seed oil has viscosity more than 50 cSt. Besides, rubber seed oil is found to be a promising alternative fuel source for compression ignition engines (Ramadhas A.S. et al., 2005). It does not need any major modification in the structure of the engine.

Table 2.2 : Properties of Rubber Seed Oil in Comparison with The Other Oils

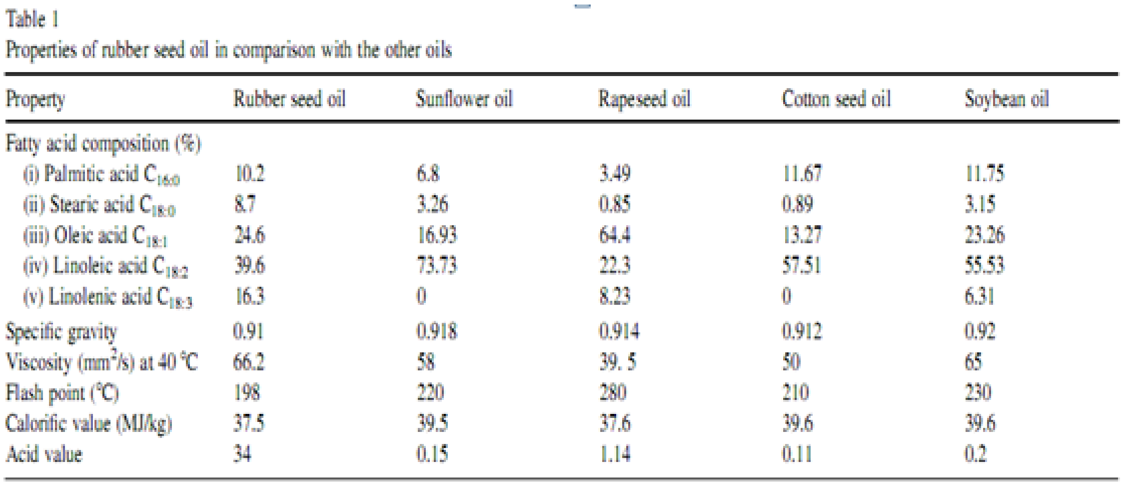

Table 1
Properties of rubber seed oil in comparison with the other oils

Property	Rubber seed oil	Sunflower oil	Rapeseed oil	Cotton seed oil	Soybean oil
Fatty acid composition (%)					
(i) Palmitic acid $C_{16:0}$	10.2	6.8	3.49	11.67	11.75
(ii) Stearic acid $C_{18:0}$	8.7	3.26	0.85	0.89	3.15
(iii) Oleic acid $C_{18:1}$	24.6	16.93	64.4	13.27	23.26
(iv) Linoleic acid $C_{18:2}$	39.6	73.73	22.3	57.51	55.53
(v) Linolenic acid $C_{18:3}$	16.3	0	8.23	0	6.31
Specific gravity	0.91	0.918	0.914	0.912	0.92
Viscosity (mm^2/s) at 40 °C	66.2	58	39. 5	50	65
Flash point (°C)	198	220	280	210	230
Calorific value (MJ/kg)	37.5	39.5	37.6	39.6	39.6
Acid value	34	0.15	1.14	0.11	0.2

Source: Ramadhas A. S. et al. (2005)

2.4 BIORENEWABLE FUELS FROM VEGETABLE OIL

The term of biofuel or biorenewable fuel (refuel) is referred to as solid, liquid or gaseous fuels that predominantly produced from biomass (Demirbas A, 2009). Production of biofuel requires to grow crops and convert them to biofuels (Hill J et al., 2006). Oxygen content is the biggest difference between petroleum feed stock and biofuels (Demirbas A, 2009). One hundred years ago, Rudolf Diesel tested vegetable oil as fuel for his engine (Shay, 1993). Biofuel are non-polluting, locally available, sustainable, accesible and reliable fuel obtain from renewable source. Many researches have shown that particulate matter, unburned hydrocarbons, carbon monoxide and sulphur levels are significantly less in the exhaust gas while using biodiesel as fuel (Ramadhas A.S. et al., 2005). After it was known that fossil fuels are finite and indeed will only suffice for a few generations, scientists have been looking for alternative fuels (Klopfenstein and Walker, 1983).

Vegetables oils from biorenewable oil seed can be used when mixed with diesel fuels. The viscosities of vegetable oils are much higher compared with usual diesel fuel and require modifications of the engine if it is used as fuels for diesel engines. Viscosity is a measure of the internal fluid friction or resistance of oil to flow, which tends to oppose any dynamic change in the fluid motion. When the temperature of oil is increased, its viscosity will decreases and it is therefore able to flow more readily. Viscosity is the most important property of biofuel since it affects the operation of fuel injection equipment, particularly at low temperatures when the increase in viscosity affects the fluidity of the fuel. There are several ways to reduce the viscosity of vegetable oils for example microemulsification, dilution, pyrolisis, catalytic cracking and transesterification. Pyrolysis process has more advantages than transesterification because it can produced liquid fuel with similar chemical components to conventional petroleum diesel fuel. Even, vegetable oils can be converted to a maximum of liquid and gaseous hydrocarbons by pyrolisis, decarboxylation, deoxygenation and catalytic cracking processes.

There has been growing interest in biodiesel, it is made from natural, renewable sources for example vegetables fat and oils. Biodiesel whether it in triacylglycerols or trans-esterified with various monohydric alcohols (Klopfenstein and Walker, 1983). Ethanol produced from biomass shows promise as a future fuel for spark ignition (SI) engines because it contains of high octane number of quality. However, ethanol also has disadvantage for example it is not suitable for compression ignition engine (CI) because of its low cetane number (Edwin Geo V. et al., 2009). Vegetable oils have comparable energy density, cetane number, heat of vaporization and stoichiometric air-fuel ratio with that of the diesel fuel (Ramadhas A.S. et al., 2005).

In the near future, vegetable oils have the potential to replace a fraction of petroleum distillates and petroleum-based petrochemicals. If compared to any other thermochemical process, pyrolysis received a significant amount of interest due to better quality of product. There are more than 350 identified oilbearing crops, among which only sunflower, safflower, soybean, cottonseed, rapeseed and peanut oils are considered as potential alternative fuels for diesel engines. Limitations to vegetable oil use are potential production and costs. Moreover, production of vegetable oil is limited by the land area available. Vegetable oil fuels are more expensive than petroleum fuel. Therefore, vegetable oil fuels are not petroleum-competitive fuel. However, due to recent increases in petroleum prices and uncertainties concerning petroleum availability, there is renewed interest in using vegetable oils as a fuel.

2.5 FATTY ACID

Fatty acid is a carboxylic acid with long hydrocarbon chain. The general formula is $R-(CH_2)_n-COOH$. The most usual length of hydrocarbon chain is 12-18 but it may vary from 10-30 carbons. The non-polar hydrocarbon alkane chain is an important counter balance to the polar acid functional group. The acid functional group dominates and gives the whole molecule a polar character in acids. It different for fatty acids, the non-polar hydrocarbon chain gives the molecule a non- polar character. Fatty acid methyl esters originating from vegetable oils and animal fats are known as biodiesel (Miao X. and Wu Q., 2006). The fatty acids contained in rubber seed oil are oleic, linoleic and linolenic acids as unsaturated fatty acids, followed by palmitic and stearic acids as saturated fatty acids. Their structures are as shown in Figure 2.2. All those fatty acids in the oil mainly composed lionleic acid, oleic acid, cetane acid by hydrolysis, gas chromatography analysis and esterification.

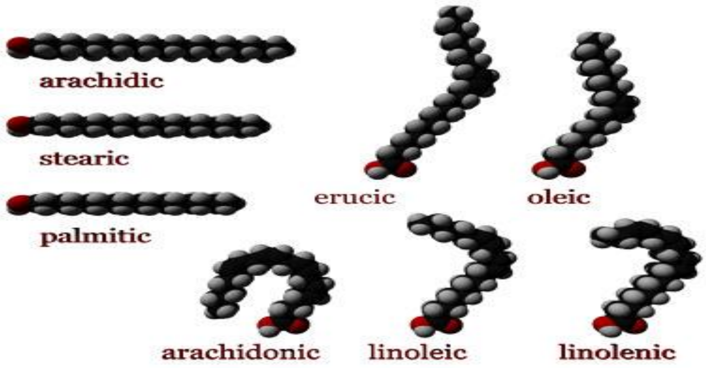

Figure 2.1 : Fatty Acid Structure

Source: Ikwuagwu O.E. et al. (2000)

The saturated fatty acids have no double bonds, while oleic acid is an unsaturated fatty acid has one double bond (also described as olefinic) and polyunsaturated fatty acids like linolenic acid contain two or more double bonds. Saturated fatty acids are evenly filled out with hydrogen, which remains solid at room temperature. Poly unsaturated fatty acids remain liquid at room temperature. If it needs to be solidified, it has to be hydrogenated, or saturated with hydrogen by breaking the carbon double bonds and attaching hydrogen.

Lauric acid (also called Dodecanoic acid) is the main acid in coconut oil (45 - 50 percent) and palm kernel oil (45 - 55 percent). Nutmeg butter is rich in myristic acid (also called Tetradecanoic acid) which constitutes 60-75 percent of the fatty-acid content. Palmitic acid (also called Hexadecylic acid) constitutes between 20 and 30 percent of most animal fats and is also an important constituent of most vegetable fats (35 - 45 percent of palm oil). Stearic acid (also called Octadecanoic Acid) is nature's most common long-chain fatty acids, derived from animal and vegetable fats. It is widely used as a lubricant and as an additive in industrial preparations. It is used in the manufacture of metallic stearates, pharmaceuticals, soaps, cosmetics, and food packaging. It is also used as a softener, accelerator activator and dispersing agent in rubbers. Oleic acid (systematic chemical name is cis-octadec-9-enoic acid) is the most abundant of the unsaturated fatty acids in nature.

2.6 ZEOLITE AS CATALYST

In the modern cracking, zeolite is used as the catalyst. zeolite which is solid catalysts offers numerous advantages over liquid catalysts. For example, it is less or no corrosion, no waste, high thermostability, easy set up of continuous processes. However, the main advantages of zeolite over conventional catalyst are they can have the great acid strength and adaptability to practically all type of catalysis processes. Many applications of zeolite have been found in the synthesis of chemicals. Zeolite is associated with positive ions such as sodium ion.

Besides, these are complex aluminosilicates, large lattices of aluminium, silicon and oxygen atoms carrying a negative charge. In catalytic cracking, zeolite is choosen to give the high percentages of hydrocarbons between 5 and 10 carbons atoms. This range is useful for petrol. It is also has some limitations. Firstly, zeolite catalyst has the great sensitivity to deactivation by irreversible adsorption or steric blockage of heavy secondary products. Besides, the impossibility of using their microporosity for the synthesis of bulky molecules. It is more difficult to exploit the shape selectivity of zeolite for their reactions than in the case of hydrocarbons. It is because the greater polarity of functional compound.

2.7 CATALYTIC CRACKING

The process in which complex organic molecules are converted to simplers molecules by breaking of carbon-carbon bonds is called cracking. Catalytic cracking of vegetable oils to produce biofuels has been studied (Pioch et al, 1993). Basic to this mechanism is the availability of strongly acidic protons at high temperature on or in a supported matrix, which can initiate the carbonium ion reaction (Hettinger, 1991). This process is widely used in chemistry and petroleum geology. It rearranges the molecular structures of hydrocarbon compounds to convert heavy hydrocarbon feedstock to lighter fractions for example gasoline, kerosene, gasoline, heating oil, liqufied petroleum gas (LPG) and petrochemical feedstock.

History shows that catalytic cracking is used around 1936. It uses catalysts to aid the process of breaking down petroleum vapour to fraction such as zeolite, silica, alumina and others. Coke in catalytic cracking is less reactive and more stabile and longer lived intermediate cations accumulate on the catalysts' active sites generating deposits of carbonaceous product. By controlled burning, such deposits need to be removed in order to restore catalyst activity.

It has been proposed that catalytic cracking of trglyceride molecules occurs at the external surface of the catalysts in order to produce small molecular size components, comprising of mainly heavy liquid hydrocarbons and oxygenate. It is assumed that the reactions predominantly occur within the internal pore structure of zeolite catalyst. Besides, catalyst acidity and pore size can give the effect to formation of aromatic and aliphatic hydrocarbons. Hydrogen transfer reactions, which are essential for hydrocarbon formation, will increase due to catalyst acidity.

Three basic functions in the catalytic cracking process:

- Reaction: Feedstock reacts with catalyst and cracks into different hydrocarbons
- Regeneration: Catalyst is reactivated by burning off coke
- Fractionation: Cracked hydrocarbon stream is separated into various product

Another latest catalytic cracking method applied is pyrolysis. Pyrolysis can be defined as the conversion of one substance into another by means of heat or by heat with the aid of catalyst. This process involves heating in the absence of air or oxygen and cleavage of chemical bonds to yield small molecules. The pyrolized material can be vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids. Liquid products of vegetable oils from pyrolysis can be used as alternative engine fuel. Vegetable oils may be converted to liquid product containing gasoline boiling range hydrocarbon. Catalyst content and temperature can give effect to the product compositions.

In pyrolysis, the high molecular materials are heated to high temperatures, so their macromolecular structures are broken down into smaller molecules and a wide range of hydrocarbons are formed. The production of gasoline like fuel catalytic pyrolysis of vegetable oil via a single step-direct process is a promising alternative route for environmentally friendly liquid fuels. The organic liquid product was composed of hydrocarbons corresponding to gasoline, kerosene, and diesel boiling point range.

The liquid products from pyrolysis have gasoline-like fractions. Table 2.3 below shows the average gasoline percentages of liquid products from pyrolysis of sunflower seed oil at different temperatures in the presence of sodium hydroxide treated aluminium oxide. Based on the table 2.3, not denied that properties of liquid products obtained from catalytic pyrolysis are similar to gasoline. The highest yields of gasoline were 53.8% for the gasoline from sunflower oil, which can be obtained from the pyrolysis with 5% catalytic runs.

Table 2.3: Average Gasoline Percentages of Liquid Products from Pyrolysis of Sunflower Seed Oil at Different Temperatures in The Presence of Aluminium Oxide

Al2O3	560K	580K	600K	620K	630K
0	5.7	9.6	11.8	13.7	16.8
1	12.5	19.3	23.7	27.9	32.5
3	17.3	23.5	28.4	32.8	38.2
4	24.9	29.4	33.9	38.7	47.4
5	33.5	39.6	42.5	48.1	53.8

Source: Demirbas A. (2009)

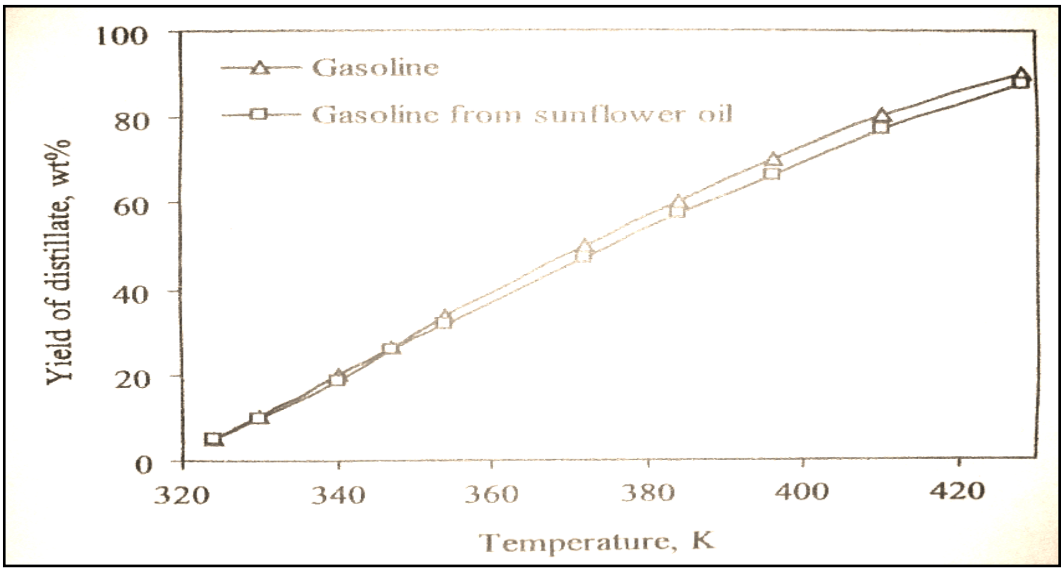

Figure 2.2 : Curves of Distillation of The Petroleum-Based Gasoline and The Gasoline from Sunflower Oil

Source: Demirbas A. (2009)

Figure 2.2 above has proving that gasoline from used lubricant oil by the catalytic pyrolysis is similar to gasoline. The petroleum-based gasoline is used for vehicles today is slightly more volatile compare with the sunflower oil gasoline.

2.8 SOXHLET EXTRACTION

Figure 2.3 : Soxhlet Extractor

Extraction is a term that is used for any operation in which a constituent of a solid or of a liquid is transferred to the solvent. In solid liquid extraction, a solvent is added to a solid. The Solid-liquid extraction is restricted to those situations in which a solid phase is present and include those operation frequently referred to as leaching, lixiviation, and washing. Solid liquid extraction is important and widely used in many industrial process. Copper is recovered from oxidized copper ores, which are usually low-grade ores containing less than 1.5 weight per cent copper, by extraction with solvents such as dilute sulphuric acid.

Soxhlet extractor is used for extraction of a lipid from solid material. It is only needed where the desired compound has a limited solubility in a solvent, and the impurity is insoluble in that solvent. Usually, simple filtration is used in order to separate the compound from the insoluble substance when the desired compound has a significant solubility in a solvent. In the extraction process, a solid material contains some of desired compound such as oil is placed inside a thimble made from thick filter paper. The extractor is connected to a boiling flask containing the extraction solvent, and a condenser is connected above the extractor. However, the boiling flask cannot be overfilled while the volume of solvent must be to four times the volume of the soxhlet chamber.

The solvent is boiled to reflux. The extractor has a bypass arm that the vapour passes through to reach the condenser, where it condenses and drips onto the sample in the thimble. When the solvent reaches the top of the siphon arm, the extract and solvent are siphoned back into the lower flask. Then, the solvent reboils while the cycle is repeated until the sample is completely extracted. The extract can get in the lower flask. This cycle may be allowed to repeat many times, over hours or days. A portion of the non-volatile compound dissolves in the solvent in each cycle. After many cycles is done, the desired compound is concentrated in the distillation flask.

Actually, this system can give several advantages for example that instead of many portions of warm solvent being passed through the sample, just one batch of solvent is recycled. Conventional Soxhlet extraction has been the most used extraction technique worldwide for a number of decades, surpassing the performance of other extraction alternatives and being used as an efficiency reference for the comparison of its conventional and new counterpart (Luque de Castro M.D and Garcia-Ayuso L.E., 1998). The soxhlet extractor is allowed to be applied to specific applications prohibited to the unchanged device.

2.9 ROTARY EVAPORATION

Evaporation is a process in which water is converted from its liquid to its vapour form. It is a type of vaporization of a liquid that only occur in the surface of a liquid. Boiling is the other type of vaporization. Besides, evaporation requires that the humidity of the atmosphere be less than the evaporating surface. There is no more evaporation at 100 %. In the evaporation process, usually large amounts of energy are required. As an example, the evaporation of one gram of water requires 600 calories of heat energy.

Rotary evaporator is used for gently and efficiently evaporating solvents from a mixture. It allows liquid solvents to be removed without excessive heating of what are often complex and sensitive solvent-solute combinations. Rotary evaporators still consist of seven primary components:

- The motor that rotates the sample (contained in either a flask or vial)
- Hot water bath to heat the sample
- The vacuum used to lower the pressure
- A vapor duct to capture the solvent
- Condenser that cools the solvent
- Flask to collect the solvent after it condenses
- A mechanism to quickly remove the sample from the hot water bath

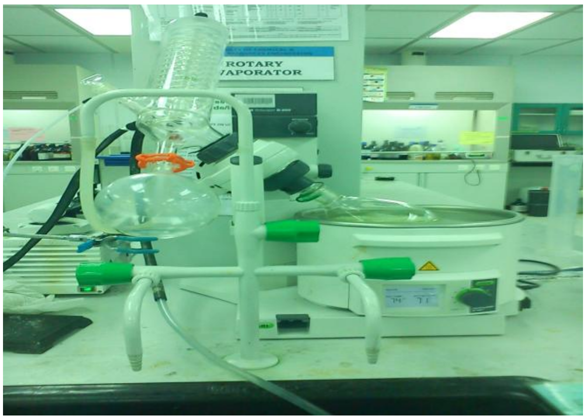

Figure 2.4 : Rotary Evaporator

It has a heated rotating vessel (usually a large flask) which is maintained under a vacuum though a tube connecting it to a condenser. In a hot water bath, the rotating flask is heated by partial emersion. When the flask is rotates, it provides improved heat transfer to the contained liquid. Besides, the rotation is also reduces the occupance of ‘bumps’ caused by superheating of liquid. Through the connecting tube, the solvent vapors can leave the flask when it reached the fixed temperature. Then, it will condensed in the condenser section. The condensed vapors drain into another flask where they are collected. Actually, this way is very efficient for removing large quantities of solvent.

Usually, the temperature of the fluid bath that used is higher than the boiling point of the solvent. This step is important because to ensure that all solvent will be evaporated in this process and can avoid overheating of the target compound that is oxidation. Oil bath is used for solvent that has temperature upper than 100 ^{0}C and water bath always is used for the solvent with boiling point lower than 100 ^{0}C. Cooling water is flowed in and out in cooling system.and to ensure the cooling system is functioning to prevent overheating. Besides, the joints of the apparatus parts will be applied with a little amount of vacuum grease to allow air to flow in.

2.10 GAS CHROMATOGRAPHY

Gas chromatography is used for separation. It employs a gas mobile phase and either a liquid (GLC)or a solid (GCS) adsorbed on a solid as a stationary phase. Besides, it is also can separate the very complex mixture and the selectivity can be adjusted in order to seperate any given pair of solutes by judicious choice of the stationary phase. However, the gas chromatography has its limitation. Its limitation is the requirement that the solute have a reasonable vapor pressure at a temperature where it is maintained. Below is the schematic diagram of a gas chromatograph :

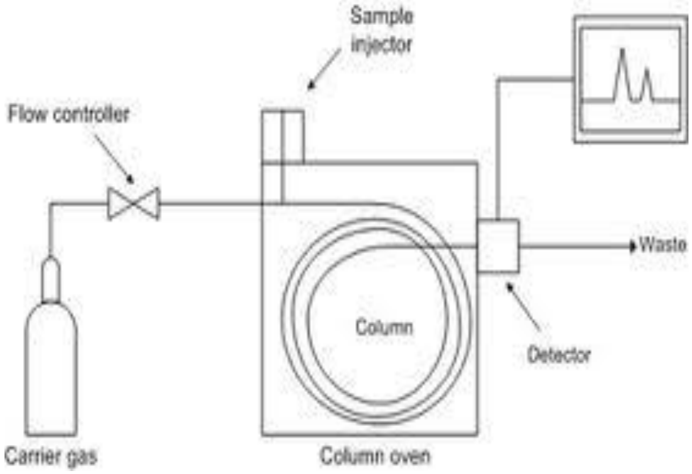

Figure 2.5 : Schematic Diagram of Gas Chromatography

Source: Omar (2006)

The carrier gas must be chemically inert. Usually, the gas that used are helium, nitrogen, argon and also carbon dioxide. Choosing the carrier gas is dependant to the type detector which is used. In the carrier gas contains a molecular sieve. It works to remove water and also others impurities.

The sample must not be to large for optimum efficiency. In injection method, a micro syringe is used to inject sample through a rubber septum into a flash vaporiser port at the head of the column. Usually the sample port is 50 °C higher than the boiling point of the least volatile component of the sample. The size ranges for sample in packed column is from 10 microliters to 20 microliters while in capillary column is around 10^{-3} μL. Split / splitless injection is used for capillary GC. The injector can be used in one of two modes, split or splitless.

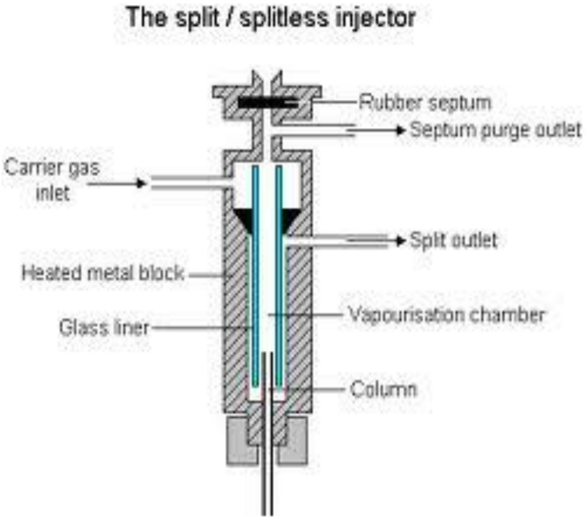

Figure 2.6 : Schematic Diagram of The Split / Splitless Injector

Source: Omar (2006)

In GC, usually the column that used is from two type of column, such as capillary and packed. Packed column has a finely divided, inert, solid support material coated with liquid stationary phase. Most packed columns are 1.5 – 10 m in length and have an internal diameter of 2 – 4 mm. For capillary column also, it has internal diameter of a few tenths of a millimetre. They can be one of two types; wall-coated open tubular (WCOT) or support-coated open tubular (SCOT).

The temperature in column must be controlled in the range of tenths of degree. The maximum column temperature is dependent to the boiling point of sample that used in the research. Temperature which is minimum can give the best resolution, but it also can increase the elution times. If a sample has a wide boiling range, then temperature programming can be useful.

Many detectors can be used in gas chromatography but the different of detectors will give the different type of selectivity. Detector is grouped into two group such as concentration dependant detectors and mass flow dependent detectors. Concentration dependant detector does not usually destroy the sample. Mass flow dependant detectors usually destroy the sample, and the signal is related to the rate at which solute molecules enter the detector. The common type of GC detectors is shown in Table 2.4 below.

Table 2.4 : Common GC Detectors

Detector	**Type**	**Support gases**	**Selectivity**	**Detectability**	**Dynamic range**
Flame ionization (FID)	Mass flow	Hydrogen and air	Most organic compounds.	100 pg	10^7
Thermal conductivity (TCD)	Concentration	Reference	Universal	1 ng	10^7
Electron capture (ECD)	Concentration	Make-up	Halides, nitrates, nitriles, peroxides, anhydrides, organometallics	50 fg	10^5
Nitrogen-phosphorus	Mass flow	Hydrogen and air	Nitrogen, phosphorus	10 pg	10^6
Flame photometric (FPD)	Mass flow	Hydrogen and air possibly oxygen	Sulphur, phosphorus, tin, boron, arsenic, germanium, selenium, chromium	100 pg	10^3
Photo-ionization (PID)	Concentration	Make-up	Aliphatics, aromatics, ketones, esters, aldehydes, amines, heterocyclics, organosulphurs, some organometallics	2 pg	10^7
Hall electrolytic conductivity	Mass flow	Hydrogen, oxygen	Halide, nitrogen, nitrosamine, sulphur		

Source: Omar (2006)

CHAPTER 3

METHODOLOGY

3.1 APPARATUS AND EQUIPMENT

The apparatus that used in this research are crucible 50 ml, flask 250 mL, beaker 100 mL, vials, filter funnel, filter papers, 0.2 μm syringe filter and syringe 25 mL, measuring cylinder 100 mL, thimble filter, anti-UV glass bottle 2000mL and micro pipette.

The equipment that used in this research are soxhlet extractor, gas chromatography, analytical balance, rotary evaporator, furnace, oven.

3.2 MATERIAL

In this research, rubber seed kernel is extracted to get the rubber seed oil and hexane (99 % purity) as non-polar solvent is used as solvent. Besides, zeolite is used in catalytic cracking process. In addition, isooctane (GC grade) which is 99 % purity is used in preparation of standard calibration curve.

3.3 PROCEDURES OF EXPERIMENT

The overall process for the production of biopetrol is shown in Figure 3.1. It has five step must be to follow.

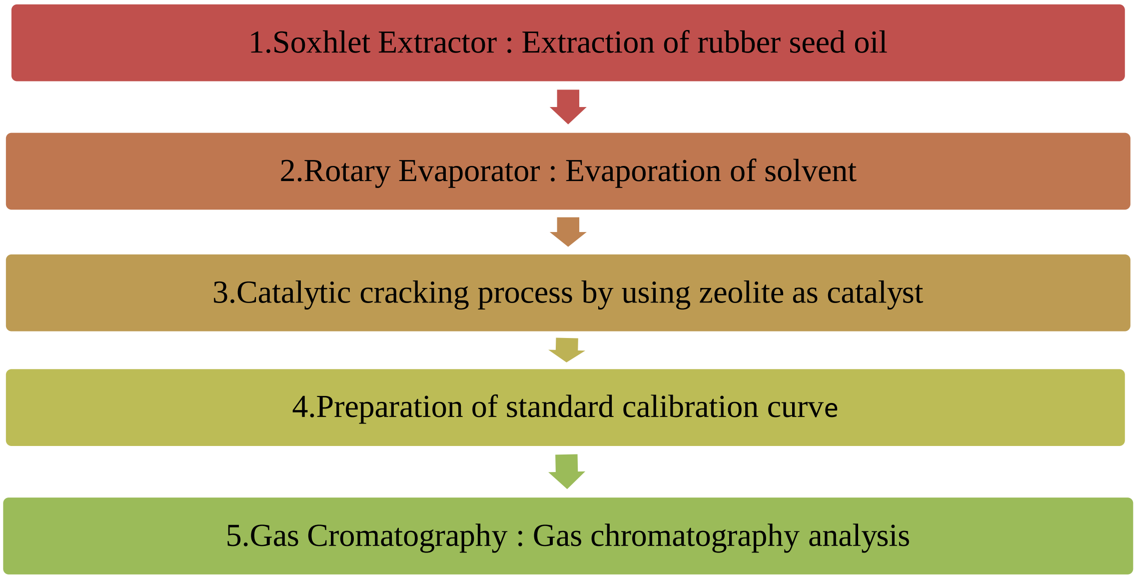

Figure 3.1 : The Overall Process of Research

3.3.1 Extraction of Rubber Seed Oil

Firstly, rubber seed are deshelled and then, it is blended into smaller particles by using a heavy duty blender. It is dried at 100°C in an oven as shown in Figure 3.2 for overnight. It is important to remove moisture inside the rubber seed particles. The blended rubber seed kernel is placed in a thimble-holder until two third portion of the thimber holder. After that, the thimble holder is inserted into siphon exit of soxhlet extractor. The hexane solvent is filled in receiving flask with mass ratio 3:1 to the rubber seed. The flask is set up with the condenser and extraction tube to get rubber seed oil. Next, the heater is switched on until the temperature of the solvent reaches about 75^0C or above hexane’s boiling point. The duration for this process is 6 hours. Then, the hexane – rubber seed oil mixture is cooled. Before using the evaporator, the solution will be transferred into anti-UV glass bottle for storage.

Figure 3.2 : Oven

3.3.2 Evaporation of Solvent

The mixture is placed inside the evaporation flask and the water bath temperature is set around 75˚C (above the boiling point of hexane which is 69˚C). The pump is turned off and the flask is stopped rotating if no more solvent is evaporated. Before the rubber seed oil is removed from the flask, the pressure in evaporation flask must be released. The liquid remaining in the flask is the pure rubber seed oil.

3.3.3 Catalytic Cracking Process Using Zeolite As Catalyst

The rubber seed oil that has already obtained from rotary evaporator is transferred into the bottle and kept in the freezer. Then, 5 g of zeolite catalyst and 25 ml of rubber seed oil is poured into a crucible. After that, the crucible is put into a glass furnace for heating. The mixture is heated at 300°C for 15 minutes. After that, the sample is filtered to obtain the oil. For the next experiment, the temperature is changed to 350°C and 400°C. Temperature is manipulated to see the effect of temperature in cracking process for production of biopetrol. After that, the sample is filtered to obtain the oil.

Figure 3.3 : Glass Furnace

Figure 3.4 : Crucibles in The Glass Furnace

3.3.4 Preparation of Standard Calibration Curve

Isooctane and hexane are prepared according to the portion in the Table 3.1 as shown below.

Table 3.1 : Composition of The Isooctane-Hexane Mixture

Vials	Composition	
	Isooctane	Hexane
1	0 %	100 %
2	20 %	80 %
3	40 %	60 %
4	60 %	40 %
5	80 %	20 %

3.3.5 Gas Chromatography Analysis.

The distilled product oil is diluted with hexane as dilution solvent in ratio (1 oil : 9 hexane). Then, using the 0.2 µm syringe filter, the samples are injected into the 1.5 mL vials. The vial is labelled and it is needed to be arranged in sequence on the auto sampler at the gas chromatography’s vial rack after standard is placed. Gas Chromatography is used to analyze the sample obtained (for every diluted mixture solutions). These are the procedures of gas chromatography that is used in this research. The condition of gas chromatography (GC) is shown in Table 3.2 below.

Table 3.2 : Gas Chromatographer (GC) condition

Temperature Column	Initial 50^{o}C, hold 3 minutes, program at 8^{o}C/min to 120^{o}C, hold 5 minutes
Detector Type	Flame Ionization Detector (FID)
Injector Temperature	250^{o}C
Detector Temperature	250^{o}C
Injection Size	1.0 µL (10:1 split)
Hydrogen Flow	35 mL/min
Air Flow	400 mL/min
Helium Make Up	35 mL/min
Carrier Gas	Helium, Compress Air, H_2, N_2
Carrier Gas Pressure	5 bar for every carrier gas

The chromatogram (peak area versus retention time) of each standard are then obtained. After that, a calibration curve (peak area versus concentration) is plotted.

3.3.6 Back Calculation Method

Because the samples must be diluted for the G.C. analysis, in order to obtain the actual concentrations for these samples, the back calculation method is applied. The equations that used for determine the isooctane concentration in each samples are state below.

- Actual Peak area of Isooctane (%)

$$= \frac{Peak\ Area\ of\ Isooctane\ (\%)}{[(100 - Peak\ Area\ of\ Hexane)\%]} \times 100\%$$

- Actual Peak Area of Isooctane (pA*s)

$$= \frac{Peak\ Area\ of\ Isooctane\ (pA * s)}{Peak\ Area\ of\ Isooctane\ (\%)} \times Actual\ Peak\ Area\ of\ Isooctane\ (\%)$$

- Actual Concentration of Isooctane (%)

$Based\ on\ equation,\ \ y = 5562x$

Where,

$y = Actual\ Peak\ Area\ of\ Isooctane\ (pA * s)$

$x = Actual\ Concentration\ of\ Isooctane\ (\%)$

From the back calculation method, assume that dilution agent not be applied directly.

CHAPTER 4

RESULT AND DISCUSSION

4.1 PREPARATION OF CALIBRATION CURVE

A calibration curve is a general method for determining the concentration of a substance in an unknown sample by comparing the unknown to a set of standard samples of known concentration. In this research, five samples that contain the mixture of isooctane and hexane is provided in order to prepare standard calibration curve. The ratio of the mixture is shown as the table below.

Table 4.1 : Composition of The Isooctane-Hexane Mixture

Vials	Composition	
	Isooctane	Hexane
1	0 %	100 %
2	20 %	80 %
3	40 %	60 %
4	60 %	40 %
5	80 %	20 %

Then, the sample is put in the gas chromatography’s vial rack for analysis. The presence of the specified chemical compound is identified through the chromatogram graph of peak area versus retention time. Each samples will take about 20 minutes to be analyzed including 5 minutes to cool it down before another sample can be analyzed. The chromatogram results for the isooctane standards are shown in Figures 4.1 to 4.5.

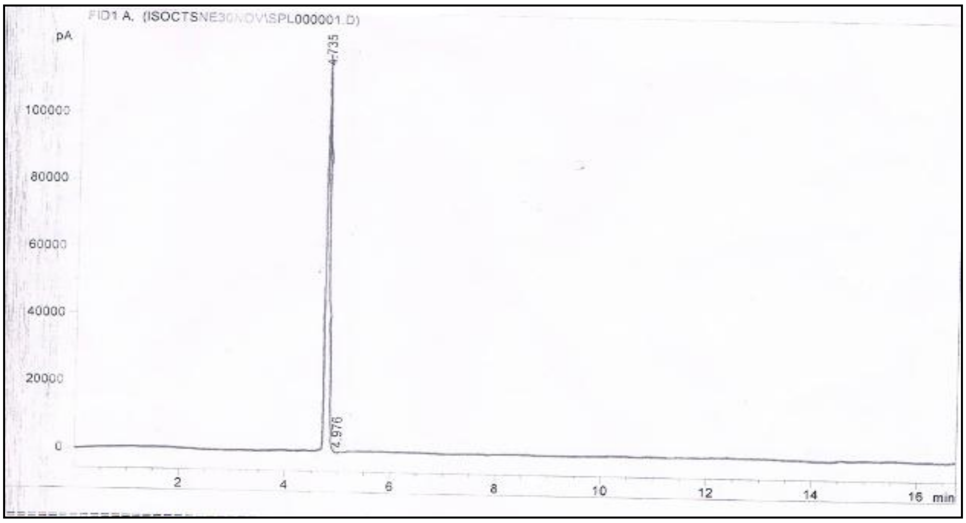

Figure 4.1 : Chromatogram of 0 % Standard Isooctane

Figure 4.2 : Chromatogram of 20 % Standard Isooctane

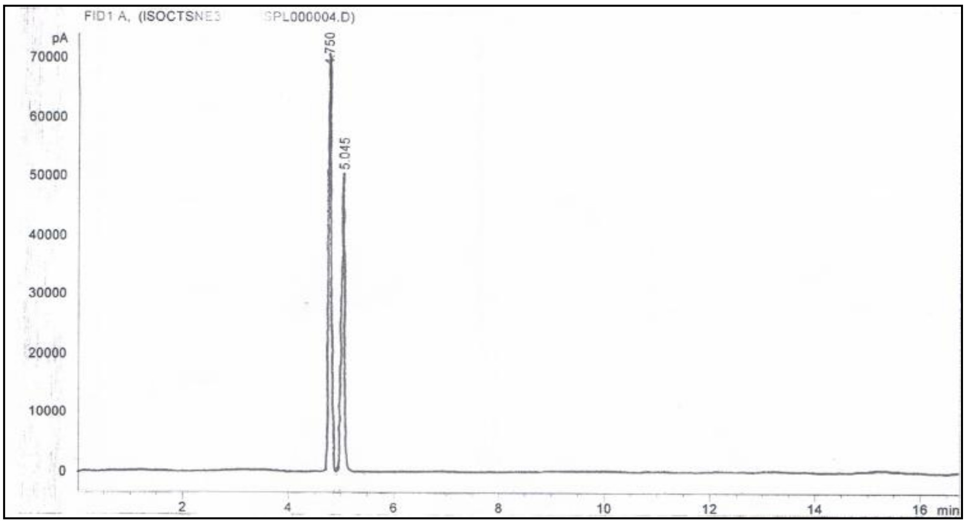

Figure 4.3 : Chromatogram of 40 % Standard Isooctane

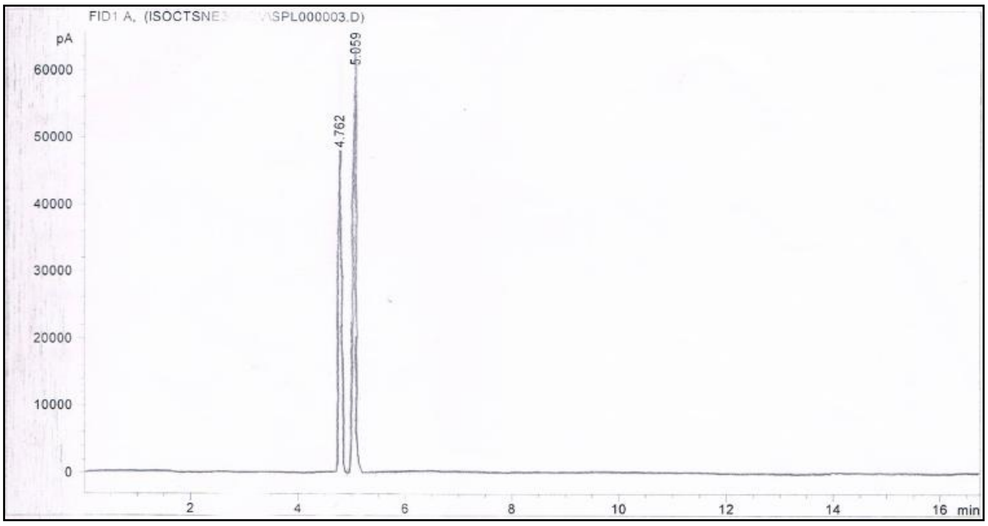

Figure 4.4 : Chromatogram of 60 % Standard Isooctane

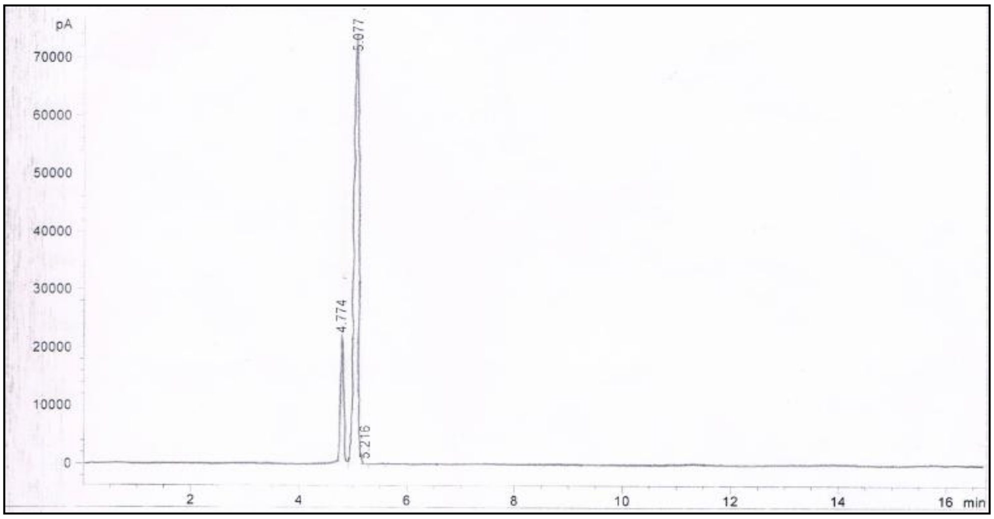

Figure 4.5 : Chromatogram of 80 % Standard Isooctane

Result of the analysis for standard sample is shown in Table 4.2. From the result obtained, the standard calibration curve is plotted with peak area (pA*s) versus concentration of the isooctane (%) as shown in Figure 4.6.

Table 4.2 : Result from Gas Chromatography

Concentration of Isooctane	Retention Time (min)	Peak Area (pA*s)
Vial 1	4.976	140.89569
Vial 2	5.034	112664
Vial 3	5.045	215759
Vial 4	5.059	322600
Vial 5	5.077	456298

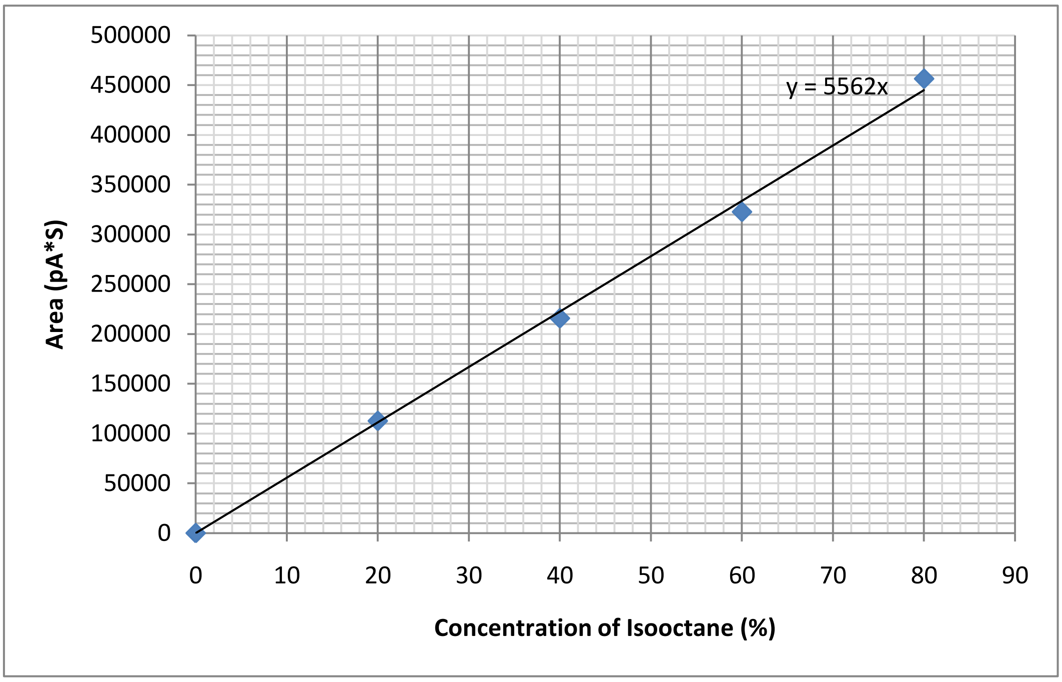

Figure 4.6 : Standard Calibration Curve

From Figure 4.6, as the concentration of isooctane increase, the peak area increases as well. The peak are of isooctane is directly proportional to the concentration of isooctane. By using the mathematical approach, the straight line is taken from the best symmetrical degree among the plotted data and the standard calibration curve equation for isooctane is:

y = 5562X (equation 1)

From this equation, the actual concentration of isooctane present in each samples can be determined by manual calculation via back calculation.

4.2 OBSERVATION

4.2.1 Cracking at 300°C

In the catalytic cracking, the amount of the rubber seed oil and zeolites are used, 25 ml and 5g respectively at temperature 300ºC. Rubber seed oil is in liquid form and light yellow at initial condition. After heat is supplied, the sample's temperature is increased while the colour of the sample changes to the darker yellow. The temperature is maintained at 300ºC for 15 minutes and a little amount of sample is taken to be analyzed by using gas chromatography. The calculations of rubber seed oil amount after cracking process are as shown below.

Mass of crucible : 33.4g
Mass of crucible + zeolites : 38.4g
Mass of crucible + zeolites + oil before cracking : 57.3g
Mass of crucible + zeolites + oil after cracking : 55.3g
Loss of oil : 57.3g – 55.3g = 2g
Mass of cracked oil : 55.3g – 38.4g = 16.9g

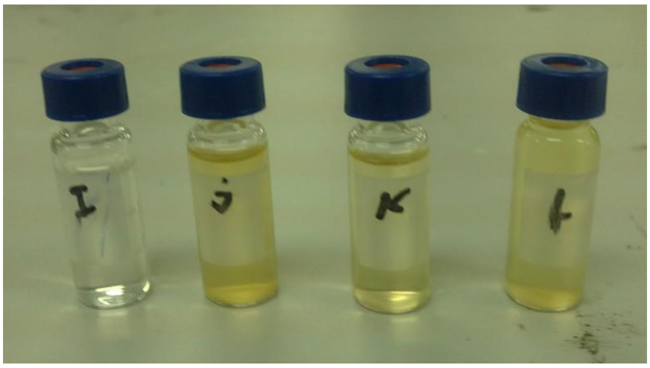

Figure 4.7 : Sample 1 (Cracking at 300°C)

4.2.2 Cracking at 350°C

In the catalytic cracking, the amount of the rubber seed oil and zeolites are used, 25 ml and 5g respectively at temperature 350ºC. Rubber seed oil is in liquid form and light yellow in colour at initial condition. After heat is supplied, the sample's temperature is increased while the colour of the sample changes to the darker yellow. The temperature is maintained at 350ºC for 15 minutes and a little amount of sample is taken to be analyzed by using gas chromatography. The calculations of rubber seed oil amount after cracking process are as shown below.

Mass of crucible : 33.2g
Mass of crucible + zeolites : 38.2g
Mass of crucible + zeolites + oil before cracking : 57.5g
Mass of crucible + zeolites + oil after cracking : 55.0g
Loss of oil : 57.5g – 55.0g = 2.5g
Mass of cracked oil : 55.0g – 38.2g = 16.8g

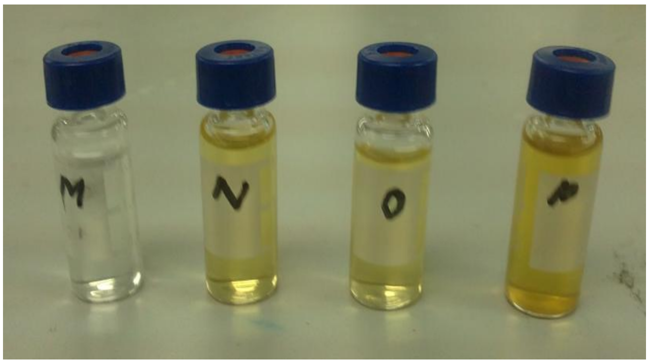

Figure 4.8 : Sample 2 (Cracking at 350ºC)

4.2.3 Cracking at 400ºC

In the catalytic cracking, the amount of the rubber seed oil and zeolites are used, 25 ml and 5g respectively at temperature 400ºC. Rubber seed oil is in liquid form and light yellow in colour at initial condition. After heat is supplied, the sample's temperature is increased while the colours of the sample change to the darkest yellow. The temperature is maintained at 400ºC for 15 minutes and a little amount of sample is taken to be analyzed by using gas chromatography. The calculations of rubber seed oil amount after cracking process are as shown below.

Mass of crucible : 33.2g
Mass of crucible + zeolites : 38.2g
Mass of crucible + zeolites + oil before cracking : 56.6g
Mass of crucible + zeolites + oil after cracking : 47.1g
Loss of oil : 56.6g – 47.1g = 9.5g
Mass of cracked oil : 47.1g – 38.2g = 8.9g

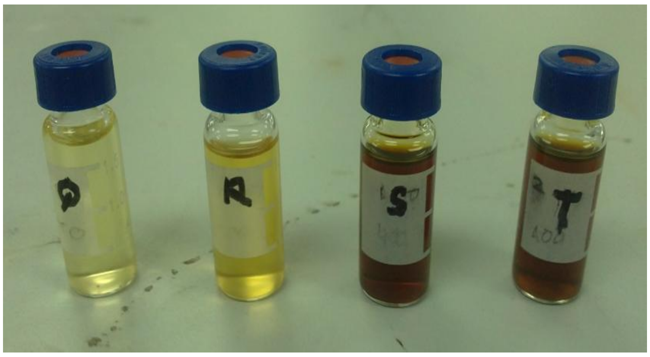

Figure 4.9 : Sample 3 (Cracking at 400°C)

4.3 ANALYSIS OF THE ACTUAL CONCENTRATION OF ISOOCTANE IN THE SAMPLE

The chromatogram of the analyzed samples is obtained. The retention time of the sample is compared to the retention time of hexane and isooctane in the chromatogram of the standard analysis. From the chromatogram of the standard analysis, isooctane exist at the retention time between 5.034 min to 5.077 min. Retention time that approach or include in the range of the chromatogram of the standard analysis is considered as an isooctane. The other peak that exist outside from the range are considered as the non desired product.

4.3.1 Chromatogram Analysis of Samples for Cracking at 300°C

Table 4.3 : Chromatogram of Cracked 300ºC Samples

Vial	Dilution Samples (%)	Isooctane			Hexane		
		Retention Time	Peak Area (Pa*s)	Area (%)	Retention Time	Peak Area (Pa*s)	Area (%)
I	1	5.060	2377.38086	0.65242	4.747	362012	99.34689
J	5	5.060	2095.47095	0.66377	4.754	313595	99.33534
K	10	5.060	2739.69238	0.65294	4.742	416851	99.34584
L	20	5.058	2352.09717	0.65021	4.747	359386	99.34807

4.3.2 Chromatogram Analysis of Samples for Cracking at 350 ºC

Table 4.4 : Chromatogram of Cracked 350ºC Samples

Vial	Dilution Samples (%)	Isooctane			Hexane		
		Retention Time	Peak Area (Pa*s)	Area (%)	Retention Time	Peak Area (Pa*s)	Area (%)
M	1	5.060	2488.19946	0.64899	4.745	380903	99.35020
N	5	5.061	2571.21069	0.64716	4.745	394724	99.35036
O	10	5.061	2718.39111	0.64668	4.743	417635	99.35114
P	20	5.061	2172.55347	0.64371	4.753	335315	99.35090

4.3.3 Chromatogram Analysis of Samples for Cracking at 400 ºC

Table 4.5 : Chromatogram of Cracked 400ºC Samples

Vial	Dilution Samples (%)	Isooctane			Hexane		
		Retention Time	Peak Area (Pa*s)	Area (%)	Retention Time	Peak Area (Pa*s)	Area (%)
Q	1	5.064	2570.78076	0.63994	4.746	399146	99.35848
R	5	5.063	2461.14844	0.63885	4.748	382783	99.36017
S	10	5.061	2117.10229	0.62973	4.753	334069	99.36885
T	20	5.064	2310.35767	0.62901	4.751	364985	99.36921

The actual concentration of Isooctane present in each sample can be obtained by backward calculation. This calculation is carried out manually knowing that the samples must be diluted with the hexane solvent before using gas chromatography. This advantage is samples are more easier to be injected into the column of analysis. The equations that used for determine the isooctane concentration in each samples are state below.

Example :

Calculation for 1% dilution (1% sample, 99% dilution agent) at 300ºC.

- Actual Peak area of Isooctane (%)

$$= \frac{0.65242}{[(100 - 99.34689)\%]} \times 100\ \% = 99.894352\ \%$$

- Actual Peak Area of Isooctane (pA*s)

$$= \frac{2377.38086}{0.65242\ \%} \times 99.894352\ \% = 364009.2586$$

- Actual Concentration of Isooctane (%)

$$364009.2586 = 5562x$$

$$x = 65.4457\%$$

The result of calculation for each samples are in the table 4.6 to 4.8 as shown below.

Table 4.6 : Experimental Matrix and Results of Each Sample for Cracking at 300°C

Vial	Dilution (%)	Isooctane Area (pA*s)	Isooctane Area (%)	Hexane Area (%)	Actual Peak Area Isooctane (%)	Actual Peak Area Isooctane (pA*s)	Actual Isooctane Concentration (%)
I	1	2377.38086	0.65242	99.34689	99.894352	364009.2586	65.4457
J	5	2095.47095	0.66377	99.33534	99.866097	315269.6042	56.6828
K	10	2739.69238	0.65294	99.34584	99.81350	418810.7412	75.2986
L	20	2352.09717	0.65021	99.34807	99.736168	360789.8348	64.8669

Table 4.7 : Experimental Matrix and Results of Each Sample for Cracking at 350°C

Vial	Dilution (%)	Isooctane Area (pA*s)	Isooctane Area (%)	Hexane Area (%)	Actual Peak Area Isooctane (%)	Actual Peak Area Isooctane (pA*s)	Actual Isooctane Concentration (%)
M	1	2488.19946	0.64899	99.35020	99.875346	382917.7368	68.8453

N	5	2571.21069	0.64716	99.35036	99.618250	395790.0818	71.1597
O	10	2718.39111	0.64668	99.35114	99.664026	418948.7881	75.3234
P	20	2172.55347	0.64371	99.35090	99.169619	334702.4279	60.1766

Table 4.8 : Experimental Matrix and Results of Each Sample for Cracking at 400°C

Vial	Dilution (%)	Isooctane Area (pA*s)	Isooctane Area (%)	Hexane Area (%)	Actual Peak Area Isooctane (%)	Actual Peak Area Isooctane (pA*s)	Actual Isooctane Concentration (%)
Q	**1**	2570.78076	0.63994	99.35848	99.753709	400732.7497	72.0483
R	**5**	2461.14844	0.63885	99.36017	99.846834	384656.6169	69.1580
S	**10**	2117.10229	0.62973	99.36885	99.7750	335435.6327	60.3085
T	**20**	2310.35767	0.62901	99.36921	99.7178	366264.104	65.8512

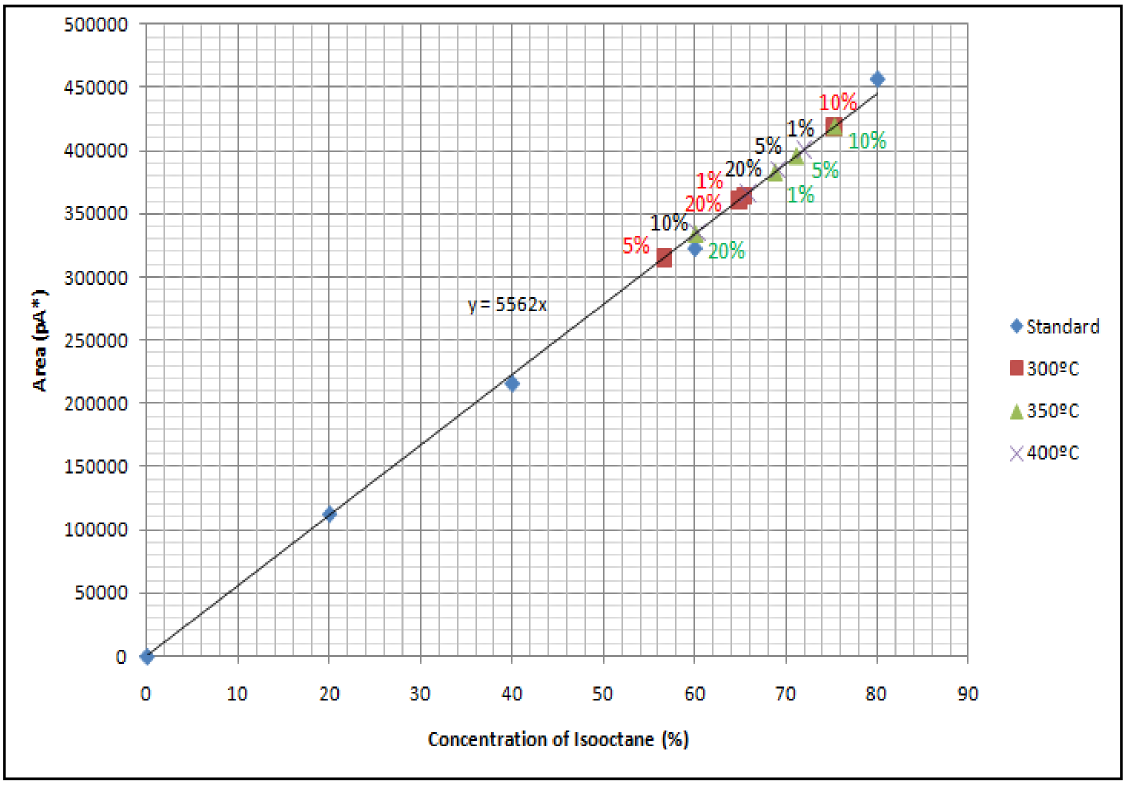

Figure 4.10 : Concentration of Actual Isooctane Present in Samples

4.4 DISCUSSION

4.4.1 Comparison of Samples

Isooctane peak area experimental for sample 1, sample 2 and sample 3 are 2739.69238, 2718.39111 and 2117.10229 at 10% dilution (10% sample, 90% dilution agent).

Sample 1 with peak area 2739.69238 has synthesized 75.2986% actual isooctane concentration while sample 2 with peak area 2718.39111 has synthesized 75.3234%. However, sample 3 with peak are 2117.10229 only synthesized 60.3085% actual isooctane concentration. All the value is taken at 10% dilution (10% sample, 90% dilution agent).

Sample 2 which is cracked at 350°C obtains the highest amount of isooctane synthesized compared with the others sample. At 10% dilution (10% sample, 90%

dilution agent), the actual isooctane concentration that obtained is 75.3234 % for sample 2, 75.2986 % for sample 1, 60.3085 % for sample 3.

4.4.2 Temperature Effect

In catalytic cracking process, heat supplied randomly attacks any of the C-C bonds in the fatty acid, which make hydrocarbon bonds fairly break in various sizes. When increasing of temperature, the formation of the small free radical also increase.

4.4.3 Catalyst Factor

There are various catalysts is used for cracking of fatty acids. The choice of the catalyst plays an important role in the cracking of fatty acids. In the catalytic cracking, catalyst will attract all the free radicals of the broken fatty acid molecules and then, combines these radicals on its surface and voids in different molecular arrangement. The isomerization occurred through this arrangement. Since zeolites are extremely active, therefore it has been tested extensively for catalytic cracking, especially of vegetable oil by several researchers. Different catalysts will lead to different product distribution of catalytic cracking. Corma *et al*. (2007) studied catalytic cracking of glycerol and sorbitol, in the presence of 6 different catalysts, including a fresh FCC catalyst, an equilibrium FCC catalyst with metal impurities (ECat), a mesoporous Al_2O_3, a USY zeolite (Y), a ZSM5-based FCC additive (ZSM5), and an inert silicon carbide (SiC). The catalysts activity (in terms of total conversion to gases, coke, and aromatics) for the conversion of glycerol increased in the order of SiC < ECat < ZSM5 < Al_2O_3 < FCC ~ USY (Corma *et al*., 2007).

The combination of acidity, hydrothermal stability, and pore size made this zeolite as the main active component of cracking catalysts. Greater surface area of catalyst increases the concentration of isooctane**.** In recent years, there have been several other studies on the production of hydrocarbons from palm oil mainly bio-gasoline/biopetrol which have been carried out using cracking catalysts in a micro-reactor. Zeolites have shown excellent performance as solid acid cracking catalysts due to their higher selectivity. One important property of zeolite is the ability to exchange cations. This is the trading of one charged ion for another on the crystal. One measure of this property is the cation exchange capacity (CEC). Zeolites have high CEC's, arising during the formation of the zeolite from the substitution of an aluminum ion for a silicon ion in a portion of the silicate framework (tetrahedral units that make up the zeolite crystal).

4.4.4 Dilution Factor

Dilution may refer to reducing the concentration of chemical. The purpose of dilution is to prevent the GC injector device from clogging and indirectly reduce the GC performance. The sample must be filtrate first before it can be analyzed by GC. In this research, hexane is used as the dilution solution. The lower percentage of dilution, the less of sample to be analyzed. When the sample of analysis is low, thus the concentration of isooctane that formed is also low. It happens because in the sample itself contains with various types of alkane such as heptane, nonane, decane and others.

In this research, 1% and 10% dilution is considered to be compared with the concentration of isooctane is produced. For the sample 1, the amount of isooctane is produced increasing at 1% and 10% dilution which are 65.4457 % and 75.2986 % while for the sample 2 are 68.8453 % and 75.3234%. However, the amount of isooctane is produced decreasing at 1% and 10% dilution for the sample 3 which are 72.0483% and 60.3085%. The sample 2 indicate the highest amount of isooctane synthesized because at initial dilution only, it has highest concentration of isooctane although at 10% dilution the value of concentration of isooctane is almost similar with sample 1.

The isooctane formed in the sample is not sure. From the peak area of each sample, concentration of isooctane can be determined with using the calibration curve. The concentration for experimental can be obtained from the calibration curve. When eliminate the dilution agent, actual peak area can be obtained. From the actual peak area, the same standard calibration curve is applied in order to obtain the actual concentration of isooctane.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

In conclusion, biopetrol can be synthesized from the rubber seed oil because the presence of many fatty acid in the rubber seed. Isooctane which is the main component in gasoline/petrol can give improvement to the efficiency and also performance of currently operating combustor. Biopetrol ensures the production of pollutant species emissions generated in combustion process is lower than usual. The method of catalytic cracking can be defined as the process to converted complex molecules to simpler molecules by breaking of carbon-carbon bond with the appearance of catalyst. Catalytic cracking with zeolites as the catalyst are chosen to give high percentages of hydrocarbons with between 5 and 10 carbon atoms that particularly useful for gasoline.

In the catalytic cracking process, three different temperature is selected which are 300ºC for sample 1, 350ºC for sample 2 and 400ºC for sample 3. Temperature factor is important in order to determine the better temperature for higher concentration of isooctane synthesized. Gas chromatography is used to analyzed the isooctane that exist in the rubber seed oil. The retention time of the sample is compared to the retention time of hexane and isooctane in the chromatogram of the standard analysis. Based on the result obtained, it shows that the sample 2 give the highest amount of isooctane produced than sample 1 and 3. It can be proved by relating the actual concentration of isooctane with two ways which are catalytic cracking temperature and percentage of dilution.

It can be said that this study successful because the desired product which is concentration of isooctane has being determined. The concentration isooctane that produced also higher which is on the range of 56% to 76%. Catalytic cracking is better compared to the thermal cracking due to the function of catalyst which enhances chemical reaction to occur faster by lowering the activation energy and increase the conversion.

5.2 RECOMMENDATION

In order to get better and more accurate result, there are some consideration need to be applied for the another study of biopetrol synthesized from the rubber seed oil on the future:

1. Analysis of sample with Gas chromatography mass spectrometry (GCMS) which combines the features of gas liquid chromatography and mass spectrometry to identify different substances within a test sample. The advantage of GCMS is it provides the standard data library.

2. Before cracking process in the furnace, make sure that outside surface of crucible is freedom from rubber seed oil. The furnace's door cannot be opened before catalytic cracking complete in order to avoid oxygen from involving reaction during catalytic cracking process. Ensure that the temperature of the furnace is low before open the door.

3. The rubber seed shell should be to reused for soxhlet extraction to get maximum amount of rubber seed oil.

4. Centrifuge is used in order to separate the high dense components and low dense components. This equipment uses of the centrifugal force for separating mixture of centrifuged sample mixtures by forming layers. The filtration process that used after catalytic cracking process takes 2 days to complete separating rubber seed oil from the catalyst. By using the centrifuge the separation duration only takes 20 minutes.

5. Glassware and apparatus should be properly cleaned before being used for experiment in order to eliminate the presence of impurities in the samples. The glassware should be disinfected and dry cleaned first before being used in the experiment. The presence of impurities can affect to the quality of the rubber seed oil that obtained.

6. The fresh rubber seed used in this study is required to prevent any loss of fatty acid contents in the rubber seeds in order to obtain a higher conversion of rubber seeds to produce rubber seed oil. The rubber seeds cannot be kept in a long time period after being collected from rubber plantation. The rubber seed kernel will reduce on the size or degraded.

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APPENDIX A
SAFETY (MSDS) FOR HEXANE

General

Synonyms: n-hexane, normal hexane, hexyl hydride
Molecular formula: C_6H_{14}
CAS No: 110-54-3
EC No: 203-777-6
EC Index No: 601-037-00-0

Physical Data

Appearance: colourless liquid
Melting point: -95ºC
Boiling point: 69ºC
Vapour density: 3 (air = 1)
Vapour pressure: 132 mm Hg at 20ºC
Specific gravity: 0.659
Flash point: -10ºF
Explosion limits: 1.2% - 7.7%
Auto ignition temperature: 453ºF

Stability

Stable. Incompatible with oxidizing agents, chlorine, fluorine, magnesium perchlorate. Highly flammable. Readily forms explosive mixtures with air. Note low flash point.

Toxicology

May cause impaired fertility. Harmful by inhalation. Irritant. May cause CNS depression. Prolonged exposure may cause serious health damage.

Risk Phrases

(The meaning of any risk phrases which appear in this section is given in appendix C)
R11, R20, R38, R48, R51, R53, R62, R65, R67.

Safety Phrases

(The meaning of any safety phrases which appear in this section is given in appendix E)
S9, S16, S29, S33, S36, S37, S61, S62

Transport Information

(The meaning of any UN hazard codes which appear in this section is given in appendix D)
UN No 1262. Hazard class 3.0. Packing group II.

Environmental Information

Harmful in the environment - may cause long-term adverse effects.

Personal Protection

Safety glasses. Effective ventilation. Remove sources of ignition from the working area.

APPENDIX B

SAFETY (MSDS) FOR 2,2,4-TRIMETHYLPENTANE

General

Synonyms: isobutyltrimetylpentane, isooctane
Molecular formula: (CH3)3CCH2CH(CH3)2
CAS No: 540-84-1
EC No: 208-759-1
Annex I Index No: 601-009-00-8

Physical Data

Appearance: colourless liquid
Melting point: -107 °C
Boiling point: 98 °C
Vapour density: 3.9
Vapour pressure: 41 mm Hg at 21°C
Specific gravity: 0.692
Flash point:-7°C
Explosion limits: 1-6%
Auto ignition temperature: 396°C

Stability

Stable, highly flammable, incompatible with oxidizing agent, reducing agents.

Toxicology

Harmful if inhaled or ingested. May be harmful through skin contact. Eye, respiratory and skin irritant.

Risk Phrases

(The meaning of any risk phrases which appear in this section is given in appendix C)

R11, R20, R22, R36, R37, R38, R50, R53, R65, R67.

Environmental Information

Very toxic to aquatic organisms may cause long-term damage to the environment.

Transport Information

(The meaning of any UN hazard codes which appear in this section is given in appendix D)

UN No 1262. Hazard class 3.0. Packing group II.

Personal Protection

Safety glasses, good ventilation, kep away from sources of ignition.

Safety Phrases

(The meaning of any safety phrases which appear in this section is given in appendix E)

S16, S26, S33, S36, S37, S39.

APPENDIX C
RISK PHRASES

Chemical data sheets available in many countries now contain codes for certain “ risk phrases”, shown as R23, R45 etc. These risk phrase codes have the following meanings:

- R1: Explosive when dry
- R2: Risk of explosion by shock, friction, fire or other sources of ignition
- R3: Extreme risk of explosion by shock, friction, fire or other sources of ignition
- R4: Forms very sensitive explosive metallic compounds
- R5: Heating may cause an explosion
- R6: Explosive with or without contact with air
- R7: May cause fire
- R8: Contact with combustible material may cause fire
- R9: Explosive when mixed with combustible material
- R10: Flammable
- R11: Highly flammable
- R12: Extremely flammable
- R14: Reacts violently with water
- R15: Contact with water liberates extremely flammable gases
- R16: Explosive when mixed with oxidising substances
- R17: Spontaneously flammable in air
- R18: In use, may form flammable/explosive vapour-air mixture
- R19: May form explosive peroxides
- R20: Harmful by inhalation
- R21: Harmful in contact with skin
- R22: Harmful if swallowed
- R23: Toxic by inhalation
- R24: Toxic in contact with skin
- R25: Toxic if swallowed
- R26: Very toxic by inhalation
- R27: Very toxic in contact with skin
- R28: Very toxic if swallowed
- R29: Contact with water liberates toxic gas.

- R30: Can become highly flammable in use
- R31: Contact with acids liberates toxic gas
- R32: Contact with acids liberates very toxic gas
- R33: Danger of cumulative effects
- R34: Causes burns
- R35: Causes severe burns
- R36: Irritating to eyes
- R37: Irritating to respiratory system
- R38: Irritating to skin
- R39: Danger of very serious irreversible effects
- R40: Limited evidence of a carcinogenic effect
- R41: Risk of serious damage to eyes
- R42: May cause sensitisation by inhalation
- R43: May cause sensitisation by skin contact
- R44: Risk of explosion if heated under confinement
- R45: May cause cancer
- R46: May cause heritable genetic damage
- R48: Danger of serious damage to health by prolonged exposure
- R49: May cause cancer by inhalation
- R50: Very toxic to aquatic organisms
- R51: Toxic to aquatic organisms
- R52: Harmful to aquatic organisms
- R53: May cause long-term adverse effects in the aquatic environment
- R54: Toxic to flora
- R55: Toxic to fauna
- R56: Toxic to soil organisms
- R57: Toxic to bees
- R58: May cause long-term adverse effects in the environment
- R59: Dangerous for the ozone layer
- R60: May impair fertility
- R61: May cause harm to the unborn child
- R62: Possible risk of impaired fertility
- R63: Possible risk of harm to the unborn child

- R64: May cause harm to breast-fed babies
- R65: Harmful: may cause lung damage if swallowed
- R66: Repeated exposure may cause skin dryness or cracking
- R67: Vapours may cause drowsiness and dizziness
- R68: Possible risk of irreversible effects

APPENDIX D
UN HAZARD CODES

- **Class 1: Explosive**

    - 1.1 Substances with a mass explosion hazard: TNT, dynamite, nitroglycerine.
    - 1.2 Substances which present a projection hazard but no mass explosion hazard.
    - 1.3 Substances which present both a fire hazard and a minor blast or projection hazard (or both) but not a mass explosion hazard.
    - 1.4 No significant hazard.
    - 1.5 Very insentive substances with a mass explosion hazard.
    - 1.6 Very insentive articles with no mass explosion hazard.

- **Class 2: Gas**

    - 2.1 Flammable gases: Gases which ignite on contact with an ignition source, such as acetylene and hydrogen.
    - 2.2 Non-flammable, non-toxic gases: Gases which are neither flammable nor poisonous. Includes the cryogenic gases/liquids (temperatures of below -100ºC) used for cryopreservation and rocket fuels, such as nitrogen and neon
    - 2.3 Toxic gases: Gases liable to cause death or serious injury to human health if inhaled, such as fluorine, chlorine, and hydrogen cyanide.

- **Class 3: Flammable liquids**

    - Packing group I, if they have an initial boiling point of 35ºC or less at an absolute pressure of 101.3 kPa and any flash point such as diethyl ether or carbon disulfide.
    - Packing group II, if they have an initial boiling point greater than 35ºC at an absolute pressure of 101.3 kPa and a flash pointless than 23ºC, such as gasoline (petrol) and acetone.

  - Packing group III, if the criteria for inclusion in Packing Group I or II are not met, such as kerosene and diesel.

- **Class 4: Flammable solids**

  - 4.1 Flammable solids: Solid substances that are easily ignited and readily combustible such as nitrocellulose, magnesium, safety or strike-anywhere matches.
  - 4.2 Spontaneously combustible: Solid substances that ignite spontaneously such as aluminium alkyls, white phosphorus.
  - 4.3 Dangerous when wet: Solid substances that emit a flammable gas when wet or react violently with water such as sodium, calcium, potassium, calcium carbide.

- **Class 5: Oxidizing substances and organic peroxides**

  - 5.1 Oxidizing agents other than organic peroxides: calcium hypochlorite, ammonium nitrate, hydrogen peroxide, potassium permanganate.
  - 5.2 Organic peroxides, either in liquid or solid form: benzoyl peroxides, cumene hydroperoxide.

- **Class 6: Toxic and infectious substances**

  - 6.1 Toxic substances
  - 6.2 Infectious substances

- **Class 7: Radioactive substances and articles: uranium and plutonium.**

- **Class 8: Corrosive substances**

  - 8.1 Acids: sulfuric acid, hydrochloric acid.
  - 8.2 Alkalis: potassium hydroxide, sodium hydroxide.

- **Class 9: Miscellaneous dangerous substances: asbestos, air bag inflators, self inflating life rafts, dry ice.**

APPENDIX E
SAFETY PHRASES

Under Ec legislation, data sheets available in the UK now contain codes for certain “safety phrases”, shown as S1, S20 etc. These phrases are also extensively used elsewhere in the world. Safety phrase codes have the following meanings:

- S1: Keep locked up
- S2: Keep out of the reach of children
- S3: Keep in a cool place
- S4: Keep away from living quarters
- S5: Keep contents under ... (appropriate liquid to be specified by the manufacturer)
- S6: Keep under ... (inert gas to be specified by the manufacturer)
- S7: Keep container tightly closed
- S8: Keep container dry
- S9: Keep container in a well-ventilated place
- S10: Keep contents wet
- S11: not specified
- S12: Do not keep the container sealed
- S13: Keep away from food, drink and animal foodstuffs
- S14: Keep away from ... (incompatible materials to be indicated by the manufacturer)
- S15: Keep away from heat
- S16: Keep away from sources of ignition - No smoking
- S17: Keep away from combustible material
- S18: Handle and open container with care
- S20: When using do not eat or drink
- S21: When using do not smoke
- S22: Do not breathe dust
- S23: Do not breathe gas/fumes/vapour/spray (appropriate wording to be specified by the manufacturer)
- S24: Avoid contact with skin
- S25: Avoid contact with eyes

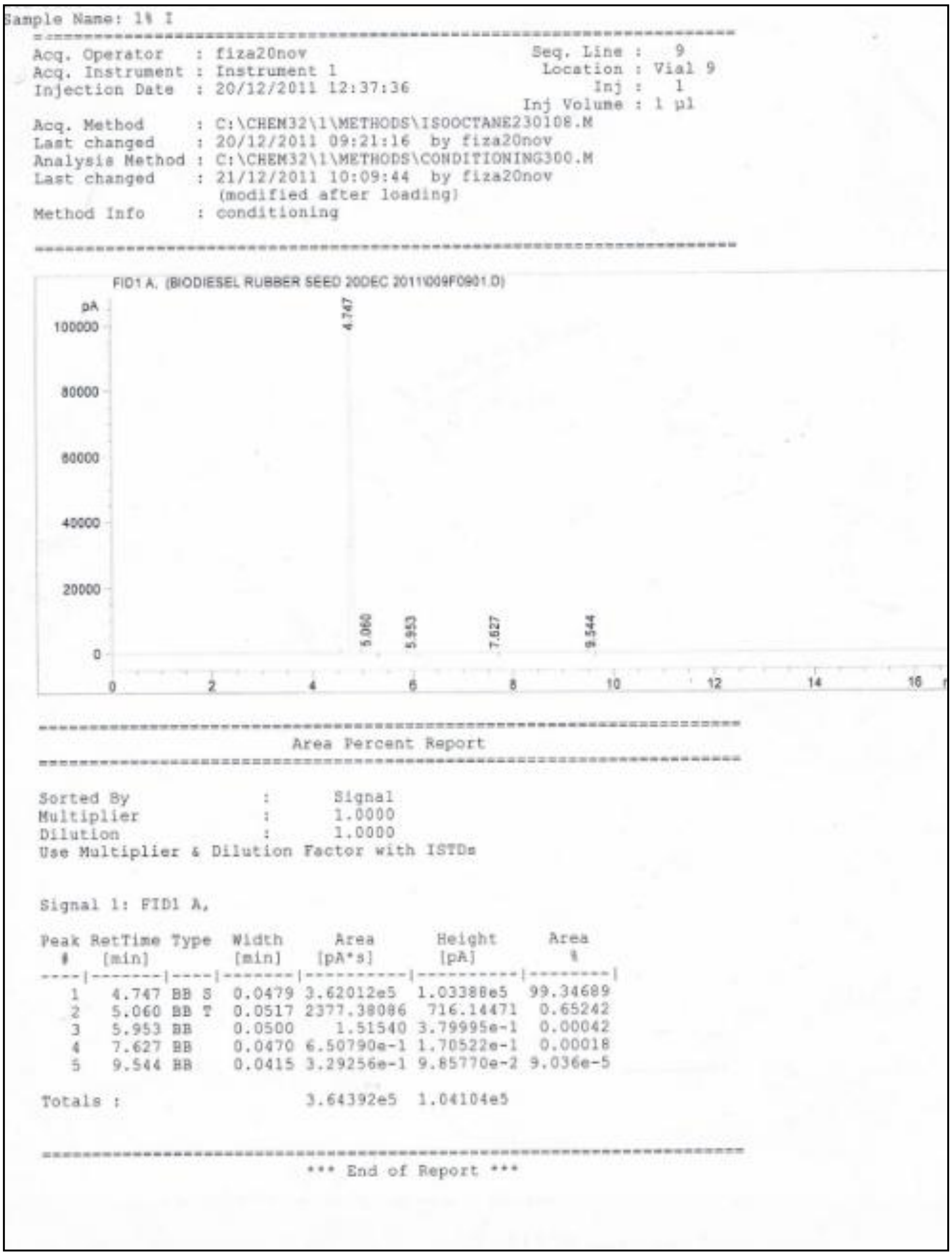
- S26: In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
- S27: Take off immediately all contaminated clothing
- S28: After contact with skin, wash immediately with plenty of ... (to be specified by the manufacturer)
- S29: Do not empty into drains
- S30: Never add water to this product
- S33: Take precautionary measures against static discharges
- S35: This material and its container must be disposed of in a safe way
- S36: Wear suitable protective clothing
- S37: Wear suitable gloves
- S38: In case of insufficient ventilation wear suitable respiratory equipment
- S39: Wear eye/face protection
- S40: To clean the floor and all objects contaminated by this material use ... (to be specified by the manufacturer)
- S41: In case of fire and/or explosion do not breathe fumes
- S42: During fumigation/spraying wear suitable respiratory equipment (appropriate wording to be specified by the manufacturer)
- S43: In case of fire use ... (indicate in the space the precise type of fire-fighting equipment. If water increases the risk add -**Never use water**)
- S45: In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
- S46: If swallowed, seek medical advice immediately and show this container or label
- S47: Keep at temperature not exceeding ... °C (to be specified by the manufacturer)
- S48: Keep wet with ... (appropriate material to be specified by the manufacturer)
- S49: Keep only in the original container
- S50: Do not mix with ... (to be specified by the manufacturer)
- S51: Use only in well-ventilated areas
- S52: Not recommended for interior use on large surface areas
- S53: Avoid exposure - obtain special instructions before use
- S56: Dispose of this material and its container at hazardous or special waste

collection point

- S57: Use appropriate containment to avoid environmental contamination
- S59: Refer to manufacturer/supplier for information on recovery/recycling
- S60: This material and its container must be disposed of as hazardous waste
- S61: Avoid release to the environment. Refer to special instructions/safety data sheet
- S62: If swallowed, do not induce vomiting: seek medical advice immediately and show this container or label where possible
- S63: In case of accident by inhalation: remove casualty to fresh air and keep at rest
- S64: If swallowed, rinse mouth with water (only if the person is conscious)

APPENDIX F

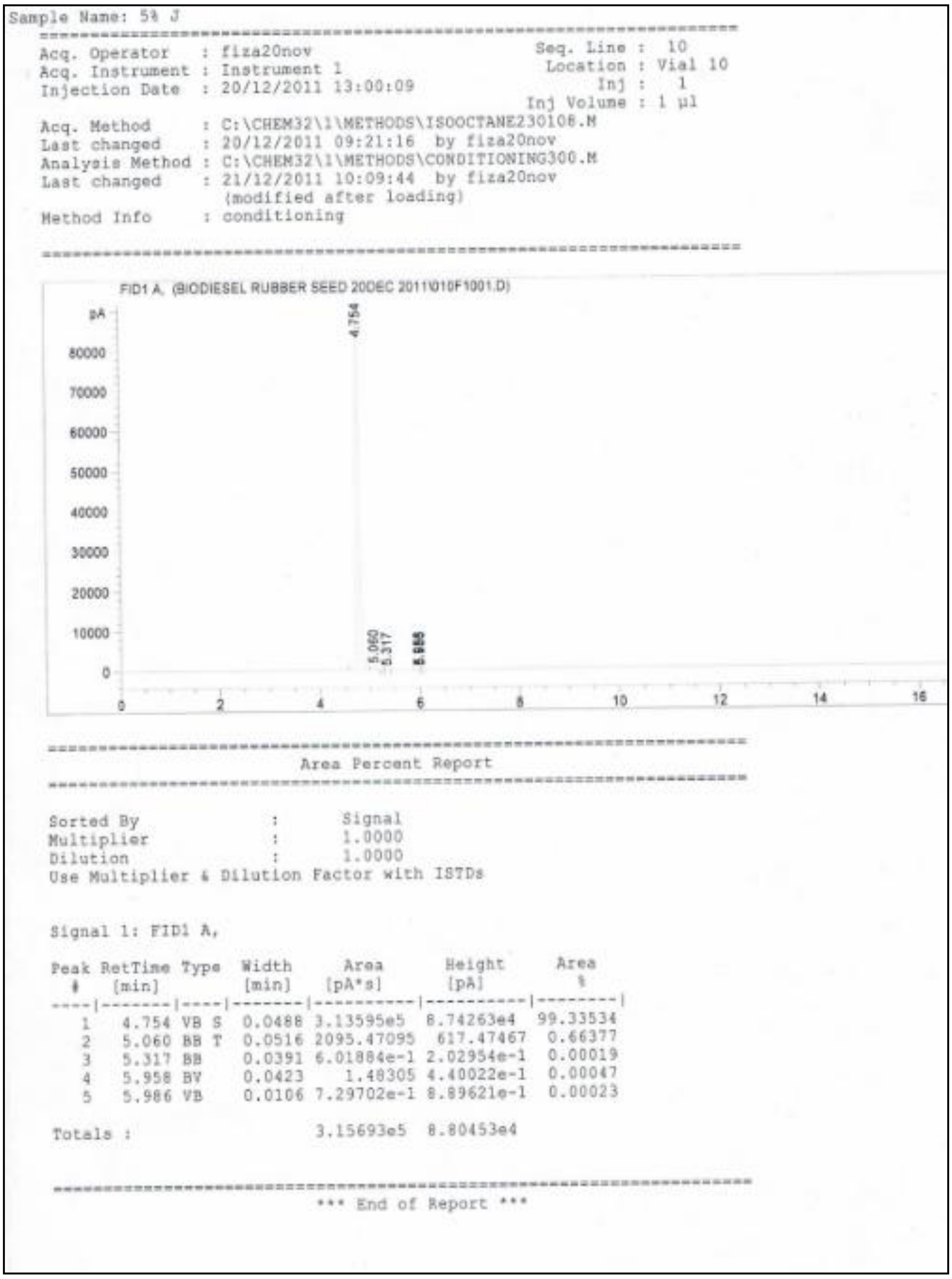
Result for sample 1 at 1% dilution (1% sample, 99% hexane)



```
Sample Name: 1% I
  =====================================================================
  Acq. Operator   : fiza20nov                          Seq. Line :    9
  Acq. Instrument : Instrument 1                        Location : Vial 9
  Injection Date  : 20/12/2011 12:37:36                      Inj :    1
                                                      Inj Volume : 1 µl
  Acq. Method     : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
  Last changed    : 20/12/2011 09:21:16  by fiza20nov
  Analysis Method : C:\CHEM32\1\METHODS\CONDITIONING300.M
  Last changed    : 21/12/2011 10:09:44  by fiza20nov
                    (modified after loading)
  Method Info     : conditioning

  =====================================================================
```

```
=====================================================================
                     Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 A,

Peak RetTime Type  Width      Area       Height      Area
  #   [min]        [min]    [pA*s]        [pA]         %
----|-------|----|-------|----------|----------|--------|
   1   4.747 BB S  0.0479 3.62012e5  1.03388e5  99.34689
   2   5.060 BB T  0.0517 2377.38086  716.14471  0.65242
   3   5.953 BB    0.0500    1.51540 3.79995e-1  0.00042
   4   7.627 BB    0.0470 6.50790e-1 1.70522e-1  0.00018
   5   9.544 BB    0.0415 3.29256e-1 9.85770e-2 9.036e-5

Totals :                  3.64392e5  1.04104e5

=====================================================================
                      *** End of Report ***
```

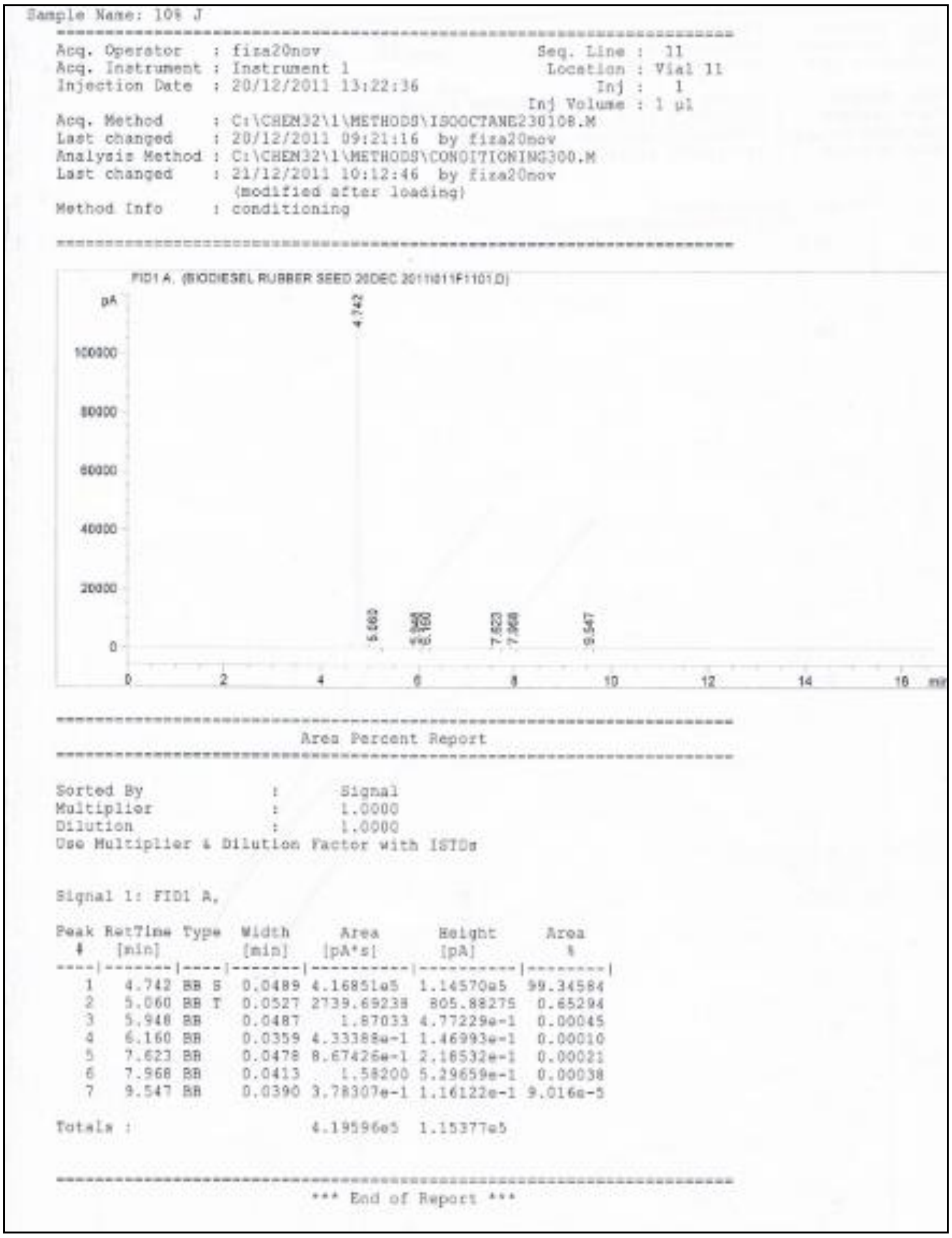
Result for sample 1 at 5% dilution (5% sample, 95% hexane)



```
Sample Name: 5% J
   =====================================================================
   Acq. Operator   : fiza20nov                          Seq. Line :  10
   Acq. Instrument : Instrument 1                        Location : Vial 10
   Injection Date  : 20/12/2011 13:00:09                      Inj :   1
                                                       Inj Volume : 1 µl
   Acq. Method     : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
   Last changed    : 20/12/2011 09:21:16  by fiza20nov
   Analysis Method : C:\CHEM32\1\METHODS\CONDITIONING300.M
   Last changed    : 21/12/2011 10:09:44  by fiza20nov
                     (modified after loading)
   Method Info     : conditioning

   =====================================================================
```

```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]         %
----|-------|----|-------|----------|----------|--------|
   1   4.754 VB S  0.0488 3.13595e5  8.74263e4  99.33534
   2   5.060 BB T  0.0516 2095.47095  617.47467  0.66377
   3   5.317 BB    0.0391 6.01884e-1 2.02954e-1  0.00019
   4   5.958 BV    0.0423    1.48305 4.40022e-1  0.00047
   5   5.986 VB    0.0106 7.29702e-1 8.89621e-1  0.00023

Totals :                  3.15693e5  8.80453e4

=====================================================================
                        *** End of Report ***
```

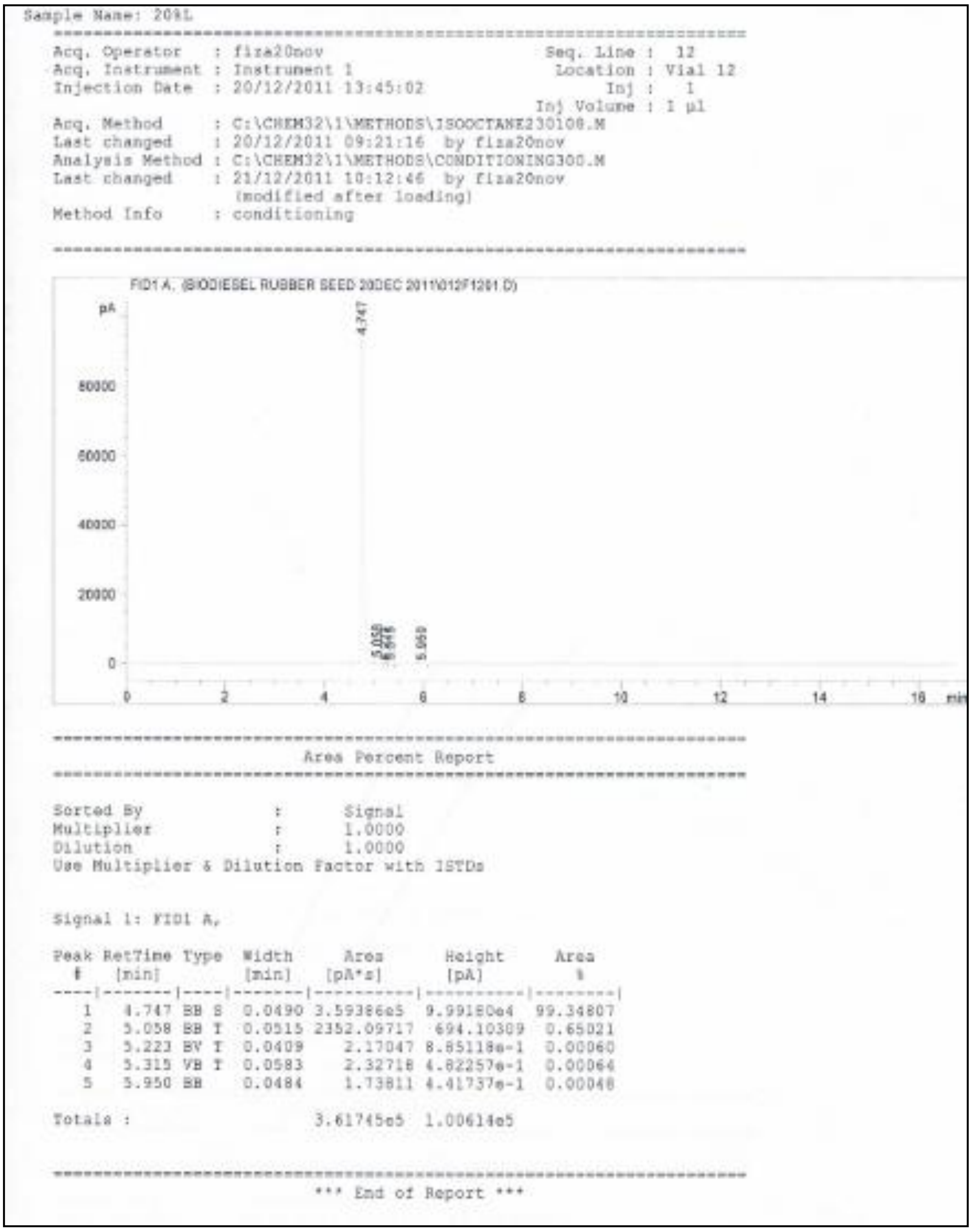
Result for sample 1 at 10% dilution (10% sample, 90% hexane)



```
Sample Name: 10% J
   =====================================================================
   Acq. Operator   : fiza20nov                        Seq. Line :  11
   Acq. Instrument : Instrument 1                      Location : Vial 11
   Injection Date  : 20/12/2011 13:22:36                    Inj :   1
                                                     Inj Volume : 1 µl
   Acq. Method     : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
   Last changed    : 20/12/2011 09:21:16  by fiza20nov
   Analysis Method : C:\CHEM32\1\METHODS\CONDITIONING300.M
   Last changed    : 21/12/2011 10:12:46  by fiza20nov
                     (modified after loading)
   Method Info     : conditioning

   =====================================================================
```

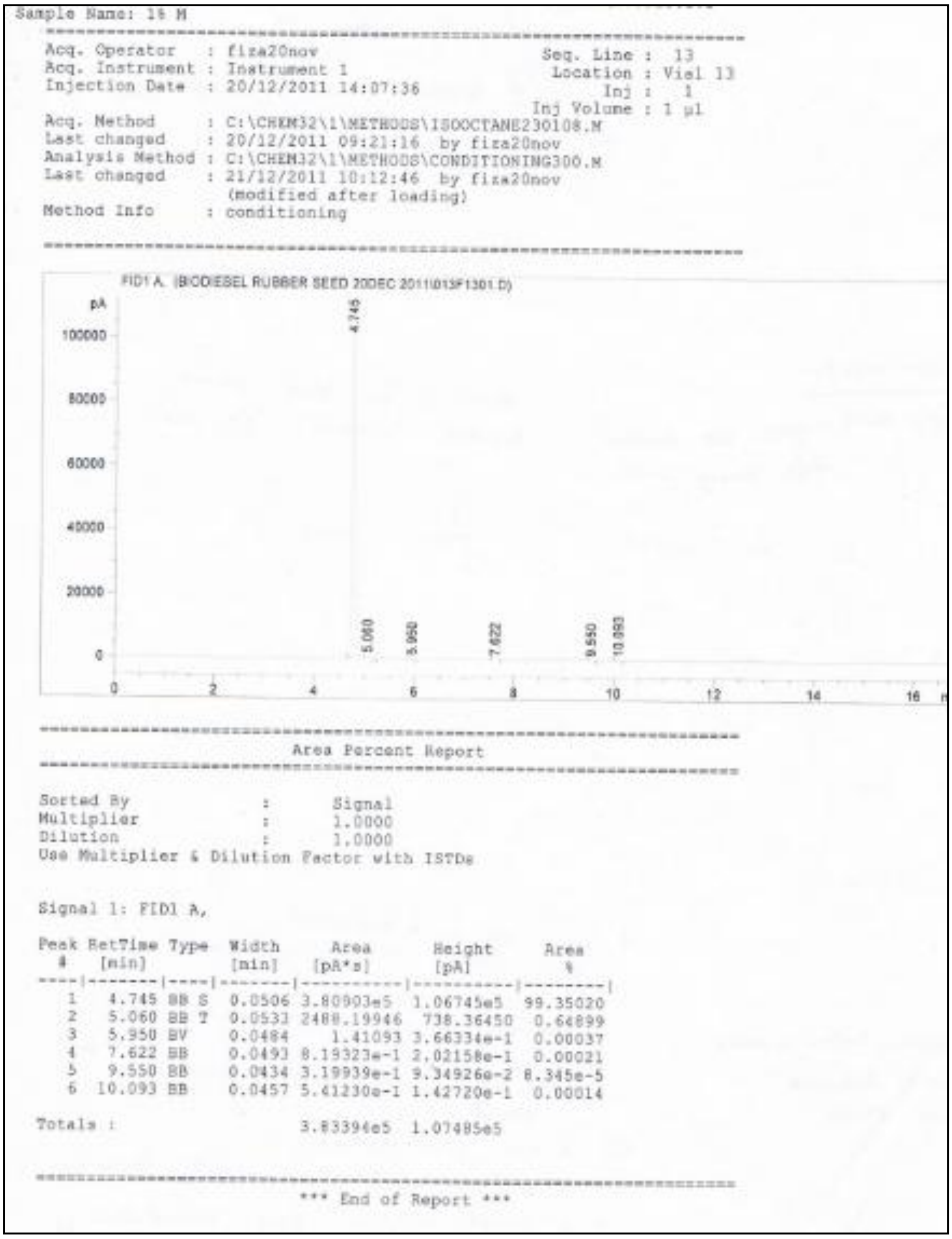
```
   =====================================================================
                         Area Percent Report
   =====================================================================

   Sorted By             :      Signal
   Multiplier            :      1.0000
   Dilution              :      1.0000
   Use Multiplier & Dilution Factor with ISTDs


   Signal 1: FID1 A,

   Peak RetTime Type  Width     Area      Height     Area
     #   [min]        [min]   [pA*s]      [pA]        %
   ----|-------|----|-------|----------|----------|--------|
      1   4.742 BB S  0.0489 4.16851e5  1.14570e5  99.34584
      2   5.060 BB T  0.0527 2739.69238  805.88275  0.65294
      3   5.948 BB    0.0487    1.87033 4.77229e-1  0.00045
      4   6.160 BB    0.0359 4.33388e-1 1.46993e-1  0.00010
      5   7.623 BB    0.0478 8.67426e-1 2.18532e-1  0.00021
      6   7.968 BB    0.0413    1.58200 5.29659e-1  0.00038
      7   9.547 BB    0.0390 3.78307e-1 1.16122e-1 9.016e-5

   Totals :                   4.19596e5  1.15377e5


   =====================================================================
                         *** End of Report ***
```

Result for sample 1 at 20% dilution (20% sample, 80% hexane)



```
Sample Name: 20%L
    =====================================================================
    Acq. Operator   : fiza20nov                        Seq. Line :  12
    Acq. Instrument : Instrument 1                      Location : Vial 12
    Injection Date  : 20/12/2011 13:45:02                    Inj :   1
                                                      Inj Volume : 1 µl
    Acq. Method     : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
    Last changed    : 20/12/2011 09:21:16  by fiza20nov
    Analysis Method : C:\CHEM32\1\METHODS\CONDITIONING300.M
    Last changed    : 21/12/2011 10:12:46  by fiza20nov
                      (modified after loading)
    Method Info     : conditioning

    =====================================================================

    =====================================================================
                             Area Percent Report
    =====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID1 A,

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [pA*s]      [pA]         %
    ----|-------|----|-------|----------|----------|--------|
       1   4.747 BB S  0.0490 3.59386e5  9.99180e4  99.34807
       2   5.058 BB T  0.0515 2352.09717  694.10309  0.65021
       3   5.223 BV T  0.0409    2.17047 8.85118e-1  0.00060
       4   5.315 VB T  0.0583    2.32718 4.82257e-1  0.00064
       5   5.950 BB    0.0484    1.73811 4.41737e-1  0.00048

    Totals :                    3.61745e5  1.00614e5

    =====================================================================
                            *** End of Report ***
```

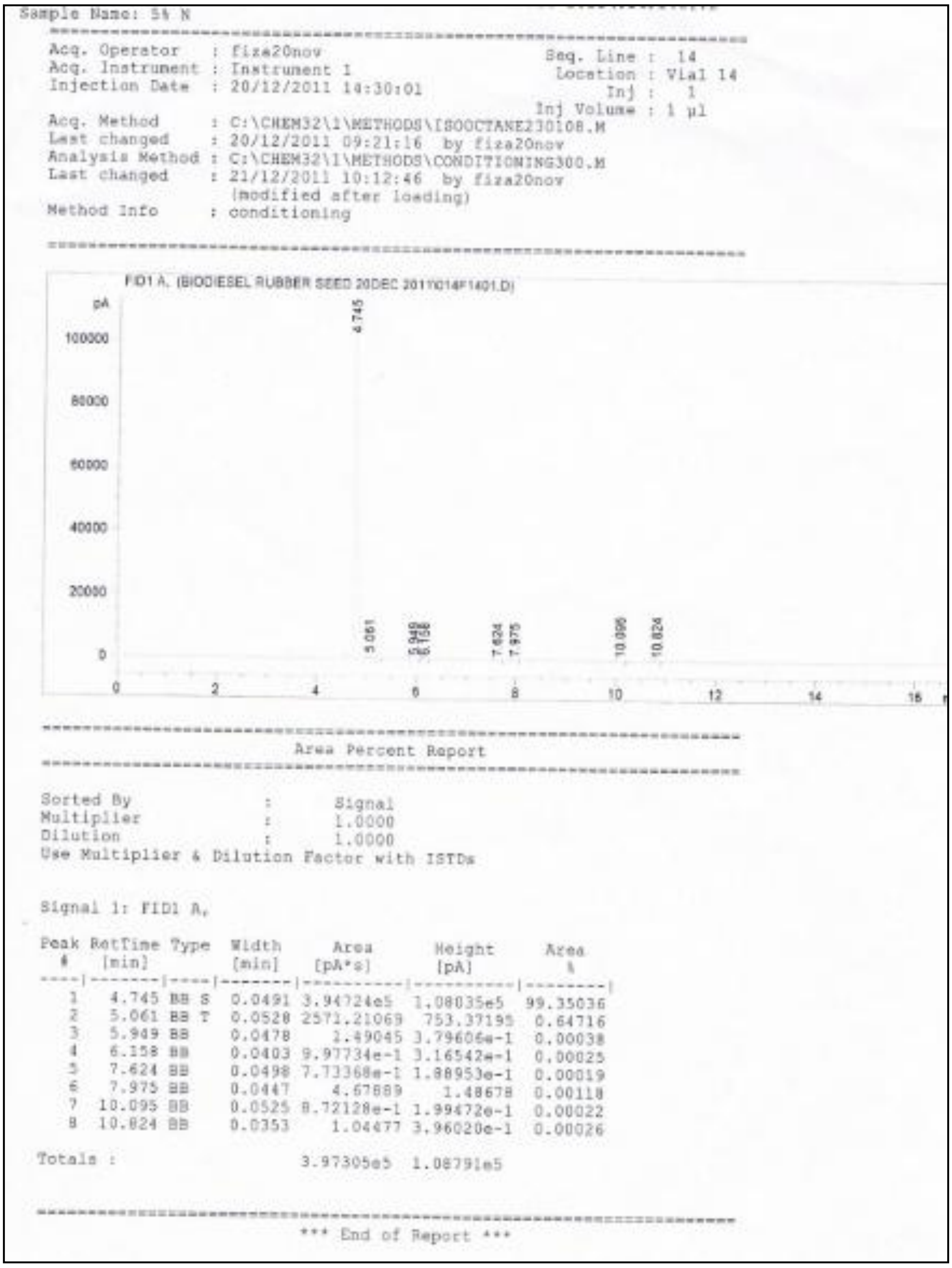
Result for sample 2 at 1% dilution (1% sample, 99% hexane)



```
Sample Name: 1% M
    =====================================================================
    Acq. Operator   : fiza20nov                         Seq. Line :  13
    Acq. Instrument : Instrument 1                       Location : Vial 13
    Injection Date  : 20/12/2011 14:07:36                     Inj :   1
                                                       Inj Volume : 1 µl
    Acq. Method     : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
    Last changed    : 20/12/2011 09:21:16  by fiza20nov
    Analysis Method : C:\CHEM32\1\METHODS\CONDITIONING300.M
    Last changed    : 21/12/2011 10:12:46  by fiza20nov
                      (modified after loading)
    Method Info     : conditioning

    =====================================================================
```

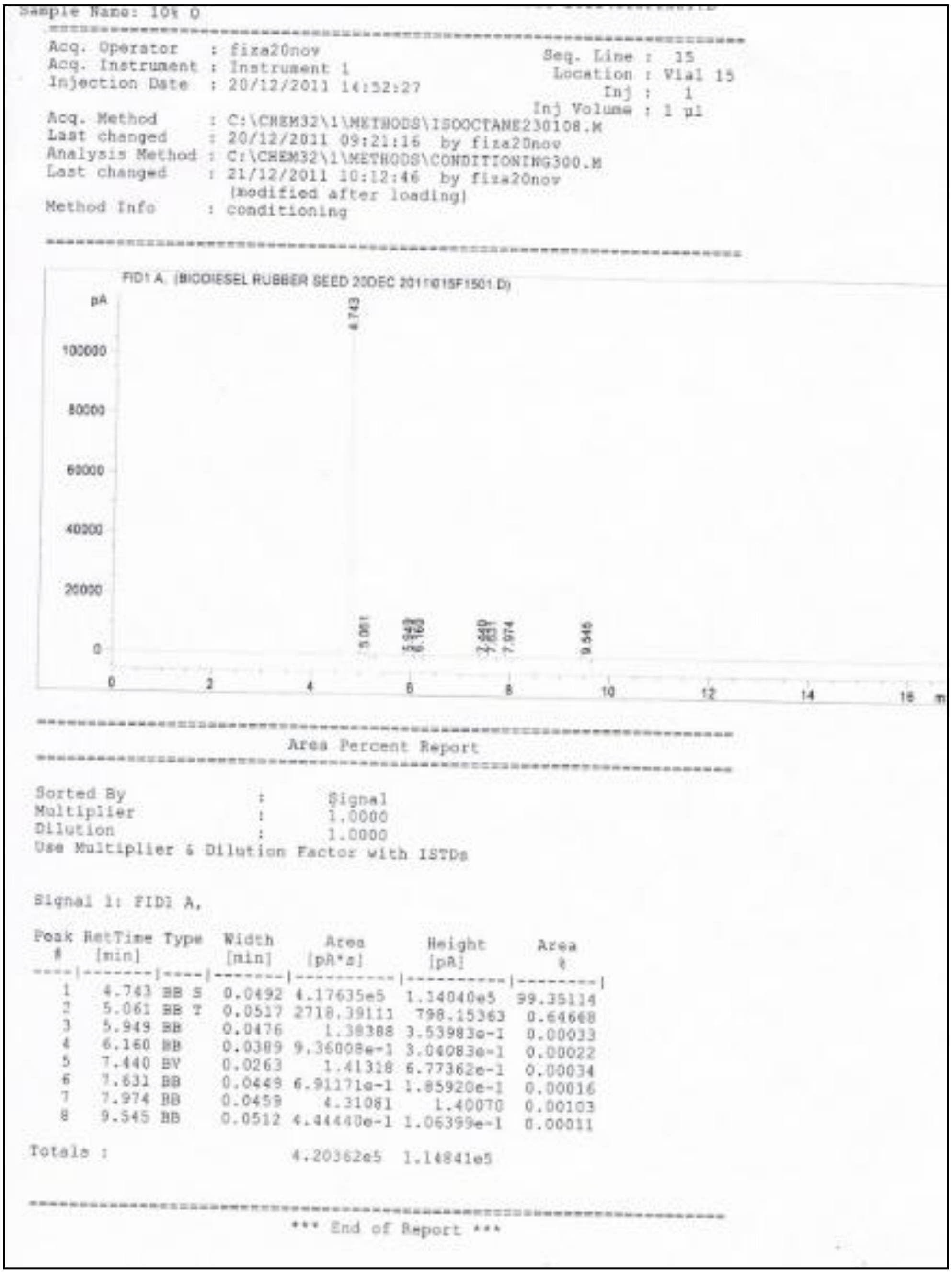
```
    =====================================================================
                              Area Percent Report
    =====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID1 A,

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [pA*s]      [pA]        %
    ----|-------|----|-------|----------|----------|--------|
       1   4.745 BB S  0.0506 3.80903e5  1.06745e5  99.35020
       2   5.060 BB T  0.0533 2488.19946  738.36450  0.64899
       3   5.950 BV    0.0484    1.41093 3.66334e-1  0.00037
       4   7.622 BB    0.0493 8.19323e-1 2.02158e-1  0.00021
       5   9.550 BB    0.0434 3.19939e-1 9.34926e-2 8.345e-5
       6  10.093 BB    0.0457 5.41230e-1 1.42720e-1  0.00014

    Totals :                  3.83394e5  1.07485e5


    =====================================================================
                              *** End of Report ***
```

Result for sample 2 at 5% dilution (5% sample, 95% hexane)



```
Sample Name: 5% N
 =====================================================================
   Acq. Operator   : fiza20nov                          Seq. Line :  14
   Acq. Instrument : Instrument 1                        Location : Vial 14
   Injection Date  : 20/12/2011 14:30:01                      Inj :   1
                                                       Inj Volume : 1 µl
   Acq. Method     : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
   Last changed    : 20/12/2011 09:21:16  by fiza20nov
   Analysis Method : C:\CHEM32\1\METHODS\CONDITIONING300.M
   Last changed    : 21/12/2011 10:12:46  by fiza20nov
                     (modified after loading)
   Method Info     : conditioning

 =====================================================================
                         Area Percent Report
 =====================================================================

 Sorted By             :      Signal
 Multiplier            :      1.0000
 Dilution              :      1.0000
 Use Multiplier & Dilution Factor with ISTDs


 Signal 1: FID1 A,

 Peak RetTime Type  Width     Area      Height     Area
   #   [min]        [min]   [pA*s]      [pA]        %
 ----|-------|----|-------|----------|----------|--------|
    1   4.745 BB S  0.0491 3.94724e5  1.08035e5  99.35036
    2   5.061 BB T  0.0528 2571.21069  753.37195  0.64716
    3   5.949 BB    0.0478    1.49045 3.79606e-1  0.00038
    4   6.158 BB    0.0403 9.97734e-1 3.16542e-1  0.00025
    5   7.624 BB    0.0498 7.73368e-1 1.88953e-1  0.00019
    6   7.975 BB    0.0447    4.67889    1.48678  0.00118
    7  10.095 BB    0.0525 8.72128e-1 1.99472e-1  0.00022
    8  10.824 BB    0.0353    1.04477 3.96020e-1  0.00026

 Totals :                  3.97305e5  1.08791e5

 =====================================================================
                         *** End of Report ***
```

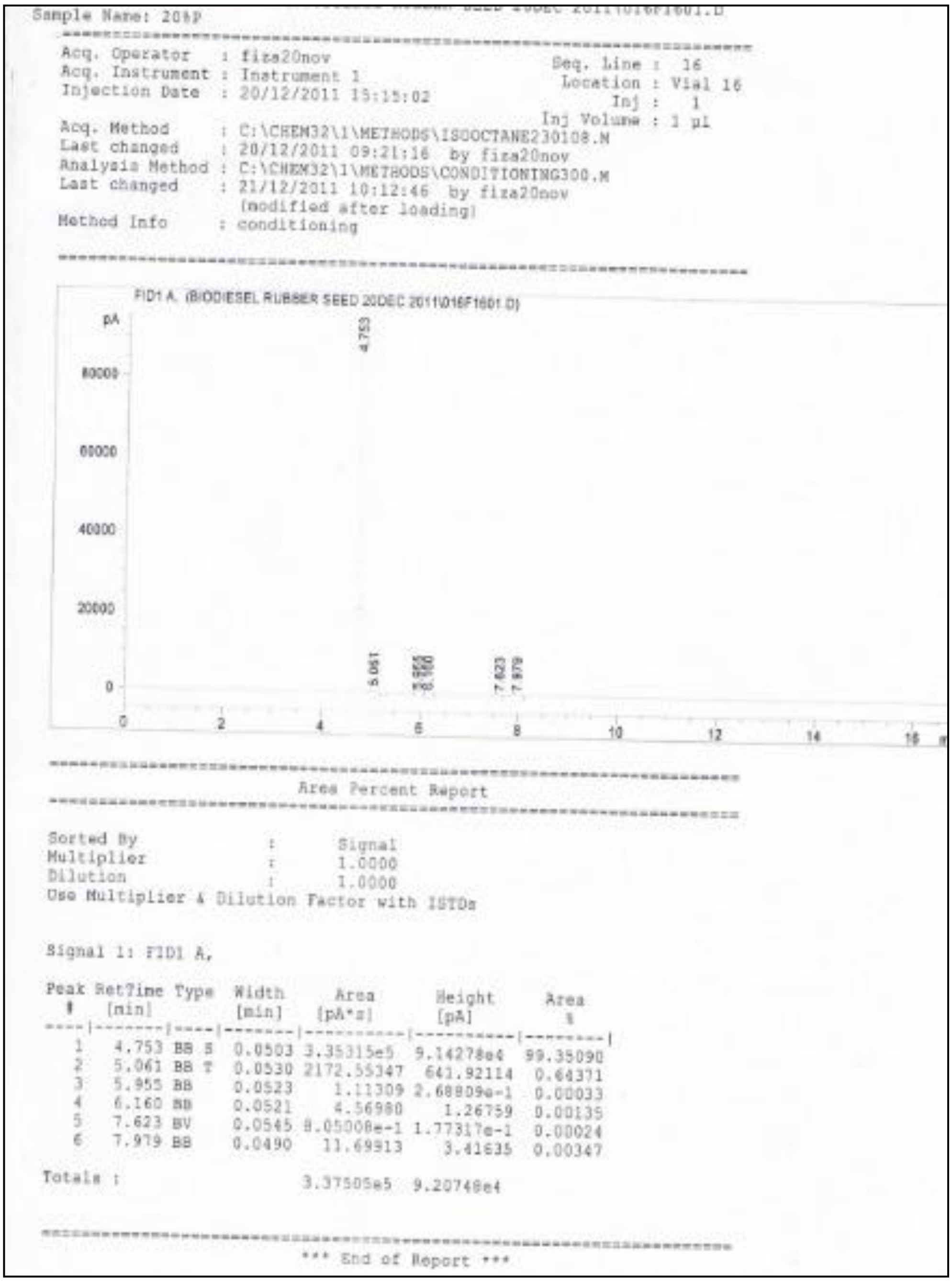
Result for sample 2 at 10% dilution (10% sample, 90% hexane)



```
Sample Name: 10% 0
=====================================================================
Acq. Operator   : fiza20nov                       Seq. Line :  15
Acq. Instrument : Instrument 1                     Location : Vial 15
Injection Date  : 20/12/2011 14:52:27                   Inj :   1
                                                 Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
Last changed    : 20/12/2011 09:21:16  by fiza20nov
Analysis Method : C:\CHEM32\1\METHODS\CONDITIONING300.M
Last changed    : 21/12/2011 10:12:46  by fiza20nov
                  (modified after loading)
Method Info     : conditioning

=====================================================================
```

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]         %
----|-------|----|-------|----------|----------|--------|
   1   4.743 BB S  0.0492 4.17635e5  1.14040e5  99.35114
   2   5.061 BB T  0.0517 2718.39111  798.15363  0.64668
   3   5.949 BB    0.0476    1.38388 3.53983e-1  0.00033
   4   6.160 BB    0.0389 9.36008e-1 3.04083e-1  0.00022
   5   7.440 BV    0.0263    1.41318 6.77362e-1  0.00034
   6   7.631 BB    0.0449 6.91171e-1 1.85920e-1  0.00016
   7   7.974 BB    0.0459    4.31081    1.40070  0.00103
   8   9.545 BB    0.0512 4.44440e-1 1.06399e-1  0.00011

Totals :                  4.20362e5  1.14841e5

=====================================================================
                       *** End of Report ***
```

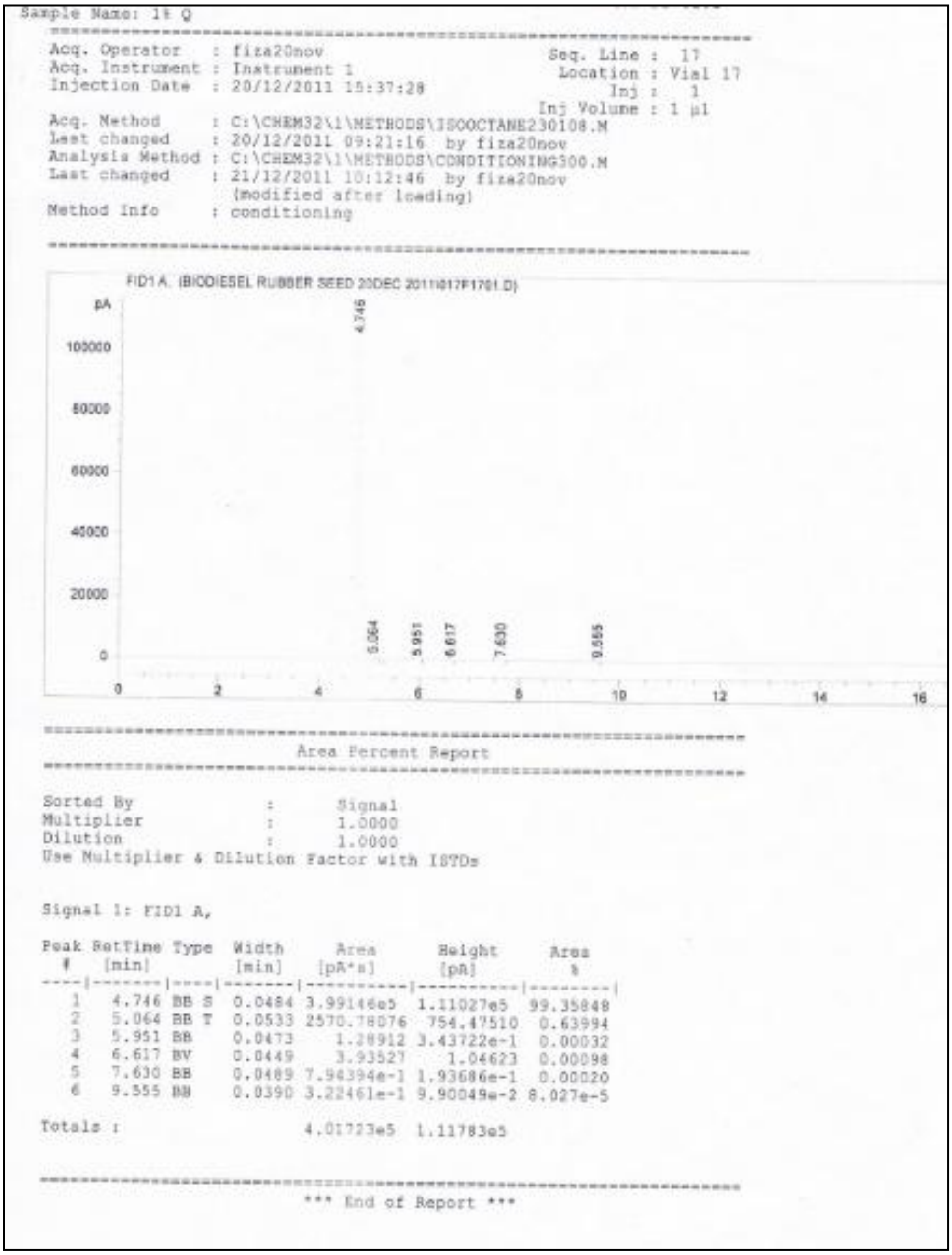
Result for sample 2 at 20% dilution (20% sample, 80% hexane)



```
Sample Name: 20%P
=====================================================================
  Acq. Operator   : fiza20nov
  Acq. Instrument : Instrument 1                    Seq. Line :  16
  Injection Date  : 20/12/2011 15:15:02              Location : Vial 16
                                                          Inj :   1
                                                   Inj Volume : 1 µl
  Acq. Method     : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
  Last changed    : 20/12/2011 09:21:16  by fiza20nov
  Analysis Method : C:\CHEM32\1\METHODS\CONDITIONING300.M
  Last changed    : 21/12/2011 10:12:46  by fiza20nov
                    (modified after loading)
  Method Info     : conditioning

=====================================================================
```

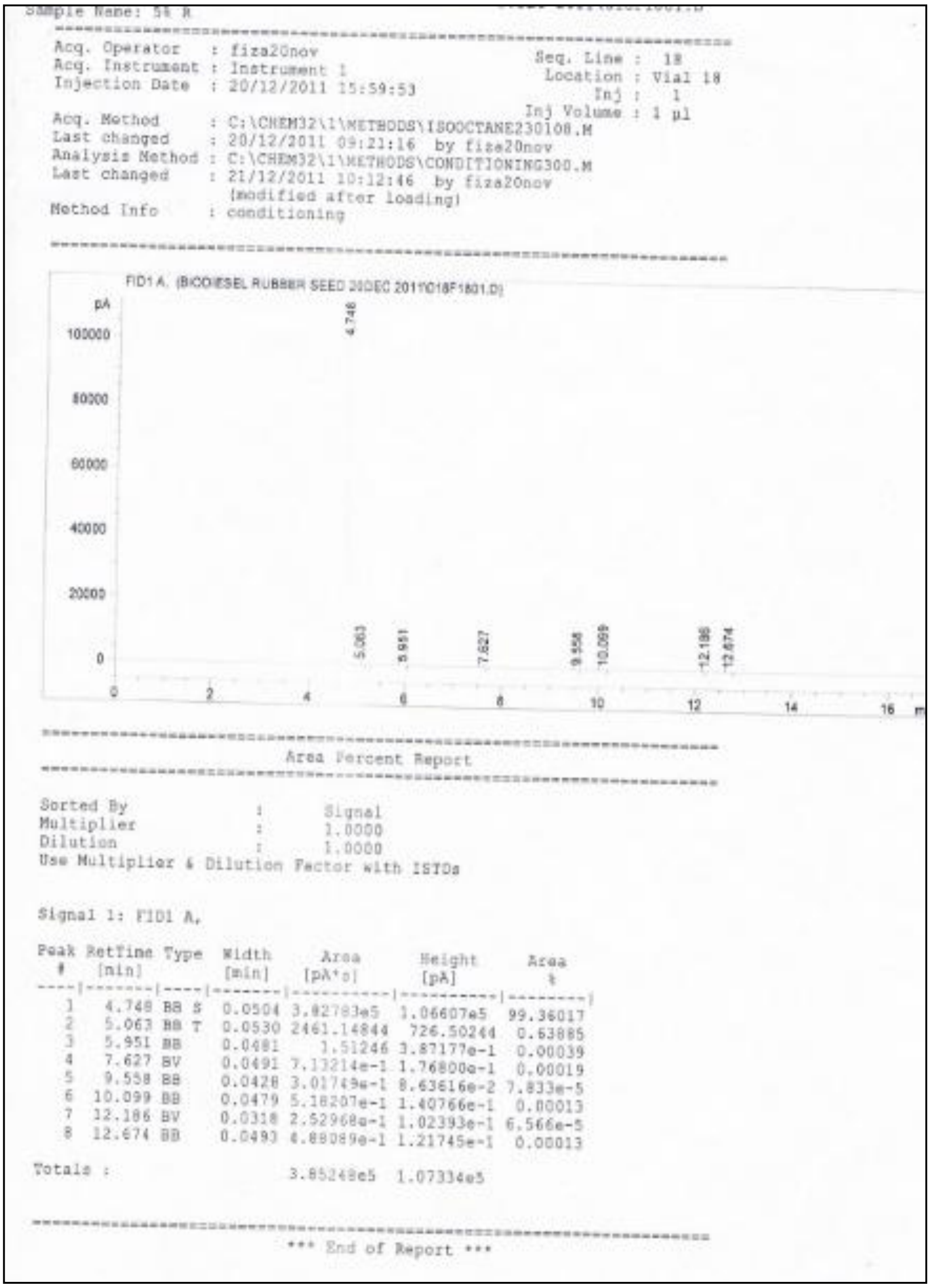
```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   4.753 BB S  0.0503 3.35315e5  9.14278e4  99.35090
   2   5.061 BB T  0.0530 2172.55347  641.92114  0.64371
   3   5.955 BB    0.0523    1.11309 2.68809e-1  0.00033
   4   6.160 BB    0.0521    4.56980    1.26759  0.00135
   5   7.623 BV    0.0545 8.05008e-1 1.77317e-1  0.00024
   6   7.979 BB    0.0490   11.69913    3.41635  0.00347

Totals :                  3.37505e5  9.20748e4


=====================================================================
                        *** End of Report ***
```

Result for sample 3 at 1% dilution (1% sample, 99% hexane)



```
Sample Name: 1% Q
  =====================================================================
  Acq. Operator   : fiza20nov                          Seq. Line :  17
  Acq. Instrument : Instrument 1                        Location : Vial 17
  Injection Date  : 20/12/2011 15:37:28                      Inj :   1
                                                      Inj Volume : 1 µl
  Acq. Method     : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
  Last changed    : 20/12/2011 09:21:16  by fiza20nov
  Analysis Method : C:\CHEM32\1\METHODS\CONDITIONING300.M
  Last changed    : 21/12/2011 10:12:46  by fiza20nov
                    (modified after loading)
  Method Info     : conditioning

  =====================================================================

  =====================================================================
                          Area Percent Report
  =====================================================================

  Sorted By             :      Signal
  Multiplier            :      1.0000
  Dilution              :      1.0000
  Use Multiplier & Dilution Factor with ISTDs


  Signal 1: FID1 A,

  Peak RetTime Type  Width     Area      Height     Area
    #   [min]        [min]   [pA*s]       [pA]        %
  ----|-------|----|-------|----------|----------|--------|
     1   4.746 BB S  0.0484 3.99146e5  1.11027e5  99.35848
     2   5.064 BB T  0.0533 2570.78076  754.47510  0.63994
     3   5.951 BB    0.0473    1.28912 3.43722e-1  0.00032
     4   6.617 BV    0.0449    3.93527    1.04623  0.00098
     5   7.630 BB    0.0489 7.94394e-1 1.93686e-1  0.00020
     6   9.555 BB    0.0390 3.22461e-1 9.90049e-2 8.027e-5

  Totals :                  4.01723e5  1.11783e5


  =====================================================================
                          *** End of Report ***
```

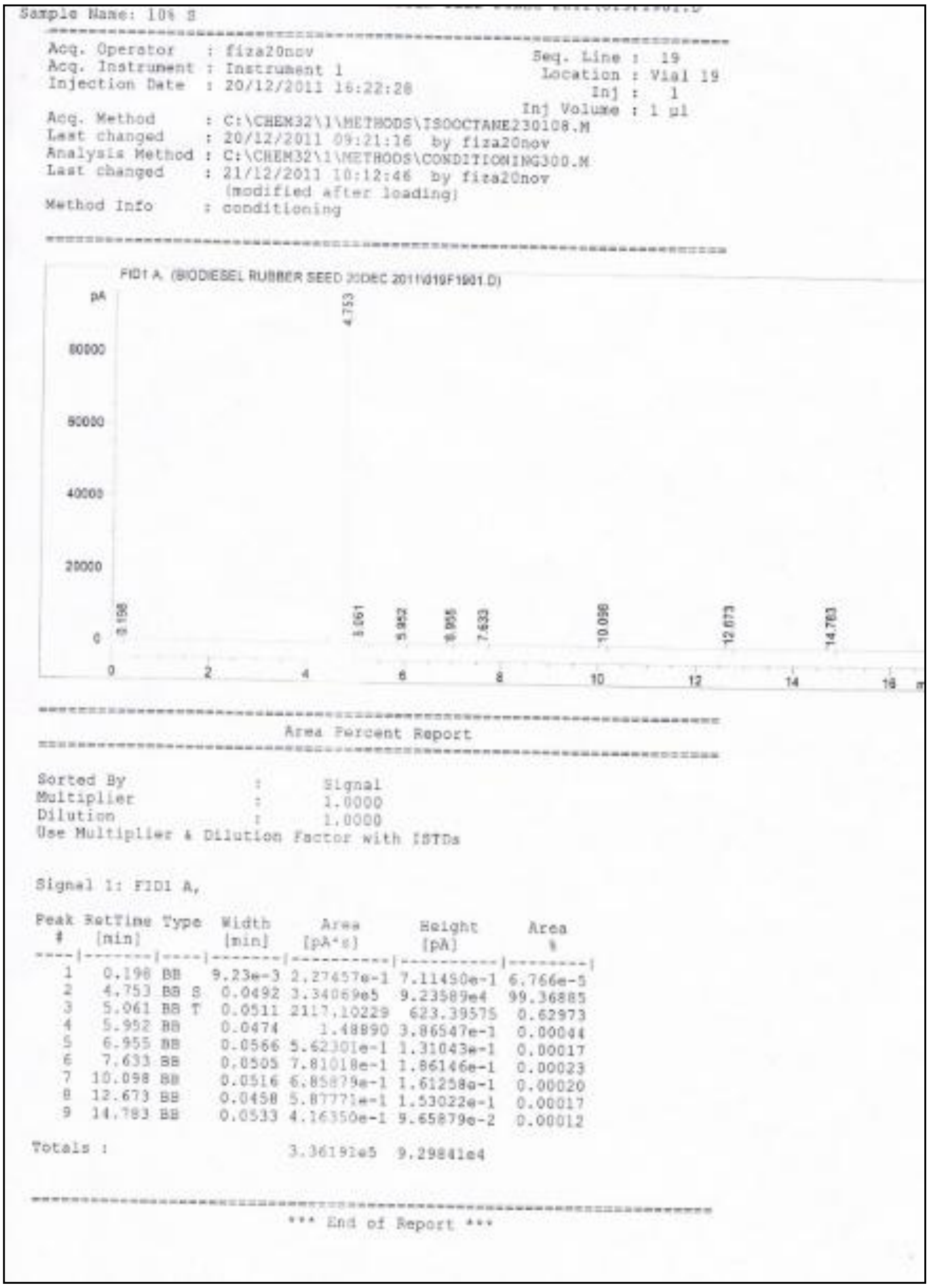
Result for sample 3 at 5% dilution (5% sample, 95% hexane)



```
Sample Name: 5% R
=====================================================================
Acq. Operator   : fiza20nov                          Seq. Line :  18
Acq. Instrument : Instrument 1                        Location : Vial 18
Injection Date  : 20/12/2011 15:59:53                      Inj :   1
                                                    Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
Last changed    : 20/12/2011 09:21:16  by fiza20nov
Analysis Method : C:\CHEM32\1\METHODS\CONDITIONING300.M
Last changed    : 21/12/2011 10:12:46  by fiza20nov
                  (modified after loading)
Method Info     : conditioning

=====================================================================
```

```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]         %
----|-------|----|-------|----------|----------|--------|
   1   4.748 BB S  0.0504 3.82783e5  1.06607e5  99.36017
   2   5.063 BB T  0.0530 2461.14844  726.50244  0.63885
   3   5.951 BB    0.0481    1.51246 3.87177e-1  0.00039
   4   7.627 BV    0.0491 7.13214e-1 1.76800e-1  0.00019
   5   9.558 BB    0.0428 3.01749e-1 8.63616e-2 7.833e-5
   6  10.099 BB    0.0479 5.18207e-1 1.40766e-1  0.00013
   7  12.186 BV    0.0318 2.52968e-1 1.02393e-1 6.566e-5
   8  12.674 BB    0.0493 4.88089e-1 1.21745e-1  0.00013

Totals :                  3.85248e5  1.07334e5

=====================================================================
                        *** End of Report ***
```

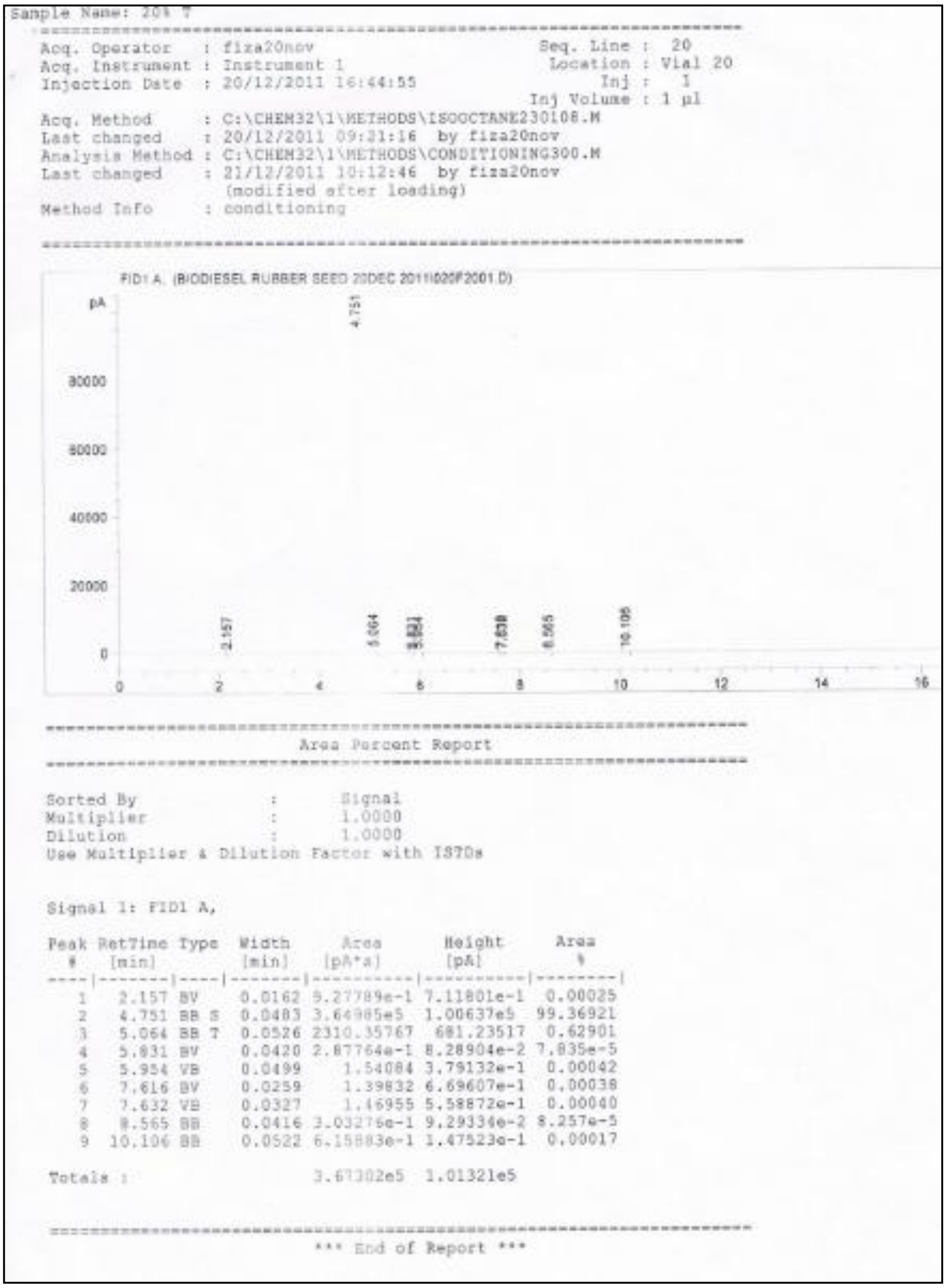
Result for sample 3 at 10% dilution (10% sample, 90% hexane)



```
Sample Name: 10% S
=====================================================================
  Acq. Operator   : fiza20nov                         Seq. Line :  19
  Acq. Instrument : Instrument 1                       Location : Vial 19
  Injection Date  : 20/12/2011 16:22:28                     Inj :   1
                                                     Inj Volume : 1 µl
  Acq. Method     : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
  Last changed    : 20/12/2011 09:21:16 by fiza20nov
  Analysis Method : C:\CHEM32\1\METHODS\CONDITIONING300.M
  Last changed    : 21/12/2011 10:12:46 by fiza20nov
                    (modified after loading)
  Method Info     : conditioning

=====================================================================
```

```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   0.198 BB   9.23e-3 2.27457e-1 7.11450e-1 6.766e-5
   2   4.753 BB S  0.0492 3.34069e5  9.23589e4  99.36885
   3   5.061 BB T  0.0511 2117.10229  623.39575  0.62973
   4   5.952 BB    0.0474    1.48890 3.86547e-1  0.00044
   5   6.955 BB    0.0566 5.62301e-1 1.31043e-1  0.00017
   6   7.633 BB    0.0505 7.81018e-1 1.86146e-1  0.00023
   7  10.098 BB    0.0516 6.85879e-1 1.61258e-1  0.00020
   8  12.673 BB    0.0458 5.87771e-1 1.53022e-1  0.00017
   9  14.783 BB    0.0533 4.16350e-1 9.65879e-2  0.00012

Totals :                  3.36191e5  9.29841e4

=====================================================================
                         *** End of Report ***
```

Result for sample 3 at 20% dilution (20% sample, 80% hexane)



```
Sample Name: 20% T
=====================================================================
Acq. Operator   : fiza20nov                      Seq. Line :  20
Acq. Instrument : Instrument 1                    Location : Vial 20
Injection Date  : 20/12/2011 16:44:55                  Inj :   1
                                               Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
Last changed    : 20/12/2011 09:21:16  by fiza20nov
Analysis Method : C:\CHEM32\1\METHODS\CONDITIONING300.M
Last changed    : 21/12/2011 10:12:46  by fiza20nov
                  (modified after loading)
Method Info     : conditioning

=====================================================================
```

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   2.157 BV    0.0162 9.27789e-1 7.11801e-1  0.00025
   2   4.751 BB S  0.0483 3.64985e5  1.00637e5  99.36921
   3   5.064 BB T  0.0526 2310.35767  681.23517  0.62901
   4   5.831 BV    0.0420 2.87764e-1 8.28904e-2 7.835e-5
   5   5.954 VB    0.0499    1.54084 3.79132e-1  0.00042
   6   7.616 BV    0.0259    1.39832 6.69607e-1  0.00038
   7   7.632 VB    0.0327    1.46955 5.58872e-1  0.00040
   8   8.565 BB    0.0416 3.03276e-1 9.29334e-2 8.257e-5
   9  10.106 BB    0.0522 6.15883e-1 1.47523e-1  0.00017

Totals :                  3.67302e5  1.01321e5

=====================================================================
                        *** End of Report ***
```