

BIOPETROL SYNTHESIZED FROM RUBBER SEED OIL THROUGH
HETEROGENEOUS CATALYTIC CRACKING USING KAOLINITE AS
CATALYST

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ABSTRACT

Biopetrol is defined as fuel which has the same characteristics with commercial petrol in term of its molecular formula. Depleting in finite fossil fuel and the valuable fatty acid loss by disposal to environment are the problematic reasons that the biopetrol should be synthesize from fatty acid. The purpose of this study is to synthesize isooctane (biopetrol) from rubber seed oil via catalytic cracking using kaolinite as catalyst. Soxhlet extraction method is used to extract the fatty acid from blended rubber seeds kernel using hexane as solvent. The catalytic cracking process is used to synthesize isooctane from distillate fatty acid and it was conducted at 98°C for 2 hours. 20 g mass of catalyst is used. The effect of different dilution of samples at 1%, 5%, 10% and 20% are studied over the concentration of isooctane. Gas chromatography is used for the qualitative and quantitative analysis of the samples. Backward calculation is applied to calculate the actual concentration of isooctane in the distilled rubber seed oil. The result showed that isooctane concentration is around 88%-108%. The factor of random reaction in cracking process, small quantity of sample, the unmodified axis peak area of impurities and also the factor of contamination effect the result obtained. This research proved that isooctane can be synthesized from rubber seed oil.

ABSTRAK

Biopetrol didefinisikan sebagai bahan bakar yang mempunyai kriteria yang sama dengan komersial petrol dari segi formula molekulnya. Bahan bakar fosil yang semakin berkurangan dan asid lemak yang tidak digunakan sepenuhnya adalah sebab biopetrol harus dihasilkan daripada asid lemak. Tujuan kajian ini adalah untuk memperolehi isooktana (biopetrol) daripada minyak biji getah melalui kaedah penguraian bermangkin dengan menggunakan agen pemangkin kaolinite. Kaedah pengekstrakan soxhlet digunakan untuk mengekstrak asid lemak daripada biji getah dengan menggunakan heksana sebagai bahan pelarut. Kaedah penguraian bermangkin digunakan untuk memperolehi isooktana daripada asid lemak dan ia dilakukan pada suhu 98°C selama 2 jam. 20g pemangkin telah digunakan. Kesan perubahan faktor pencairan isooktana kepada heksana pada 1%, 5%, 10% dan 20% dikaji terhadap penghasilan biopetrol. Alat Gas Kromatografi telah digunakan untuk kualitatif dan kuantitatif analisis semua sampel. Pengiraan semula kepekatan isooktana tanpa pencairan heksana digunakan untuk mengira kepekatan sebenar isooktana di dalam didihan minyak biji getah. Keputusan menunjukkan kepekatan isooktana adalah di antara 88%-108%. Faktor-faktor seperti penguraian secara rawak, kuantiti bahan ujikaji yang sedikit, tidak mengubahsuai paksi dan pencemaran bahan uji kaji mempengaruhi keputusan yang diperolehi. Kajian ini membuktikan bahawa isooktana boleh diperolehi daripada minyak biji getah.

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LIST OF SYMBOLS

P	-	Pressure
m	-	Mass
ΔH	-	Enthalpy change of reaction
ΔS	-	Entropy change of reaction
ΔG	-	Energy change of reaction
T	-	Temperature
ρ	-	Density
μ	-	Viscosity of liquid (Pa.s)
h	-	Heat transfer coefficient
$^{\circ}\text{C}$	-	Degree Celsius
kg	-	Kilogram
K	-	Degree Kelvin
m	-	Meter
L	-	Liter
%	-	Percentage

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Biofuels in the solid form has been in use ever since man discovered fire. Wood was the first form of biofuel that was used even by the ancient people for cooking and heating. Biofuel had been used since a very long time for the production of electricity. This form of fuel was discovered even before the discovery of the fossil fuels, but with the exploration of the fossil fuel like gas, coal, and oil, the production and use of biofuel suffered a severe impact. With the advantages placed by the fossil fuels they gained a lot of popularity especially in the developed countries.

With the increased supply the geopolitical and economic interest in biofuel faded away. A serious fuel crisis again hit the various countries during the period of 1973 and 1979, because of the geopolitical conflict. Thus Organization of the Petroleum Exporting Countries, (OPEC) made a heavy cut in exports especially to the non OPEC nations. The constant shortage of fuel attracted the attention of the various academics and governments to the issues of energy crisis and the use of biofuels. The twentieth century came with the attention of the people towards the use of biofuels. . Nowadays, liquid biofuel have been used in the automotive industry since its inception. Biofuels for transport, including bioethanol, biodiesel, biogas and biopetrol have enormous potential to displace a depletion amount of conventional fossil-derived fuels around the world over the next decades. Some of the main

reasons for the people shifting their interest to biofuels were the rising prices of oil, emission of the greenhouse gases and interest like rural development.

In the recent years, systematic efforts have been made by several researchers to use the various vegetable oils as fuel in compression ignition engines. The calorific value of vegetable oil is comparable to that of diesel. Instead of environmental friendly, the usage of biofuel also can improve the engine efficiency. The advantages in biofuels have been contributes to this research based on production of biopetrol from rubber seed oil.

1.2 Research Background

Production and age of renewable fuels for transportation purposes are the approaches to establish sustainable energy for the world in future. A renewable fuel contributes to reduce global climate change. Current research developed by a research team of the Department of Chemical Engineering in Universiti Teknologi Petronas, (UTP) was synthesized biodiesel from rubber seeds in Malaysia. It states that rubber-seed oil has high content of free fatty acids (FFAs). Besides, there was between 30% and 40% of oil in rubber seeds and 1kg of rubber seeds could produce between 300ml and 400ml of biodiesel fuel (M.T. Azizan, 2008). The natural form of rubber seed oil is highly acidic functional groups such as carbonyl, oleifinic unsaturation, ester, glyceryl, methylene and terminal methyl are present in rubber seed oil. While, A.S Ramadhas at 2004 stated in his journal, Rubber seed kernels (50–60% of seed) contain 40–50% of brown color oil. It can produce the high quality of biodiesel fuel at low cost through two steps of transesterification.

1.3 Biopetrol Synthesized from Rubber Seed's Fatty Acids

Soxhlet extraction method is a conventional method for extraction and it is suitable for lab scale extraction. In this method, rubber seeds powder are extracted many times using hexane as a non polar solvent. Then the fatty acid which is extracted from rubber seeds powder will be converted into biopetrol using catalytic cracking method using kaolinite as catalyst. Catalytic cracking method has been used

widely in petroleum refineries and the result from catalytic cracking shows higher octane number than the thermal cracking.

Commonly, natural triglycerides present in vegetable oil are extracted into several oil components using transesterification route but it generates a large amount of glycerin (byproduct) thus difficult to purify. Therefore, catalytic cracking method using heterogeneous catalyst is applied because it is easier in separation process. This research will derive rubber seed's fatty acid into biopetrol at 1 atm and 98°C. In this case, fatty acid has been chosen for conversion into isooctane which is the dominant component in biopetrol since those fatty acids contain low sulfur and nitrogen.

Kaolinite also is chosen as catalyst in catalytic cracking process because it contains the element of aluminosilicate which possesses a higher catalytic activity and it has more stability, as well as other current aluminosilicate compound in petroleum refining.

In order to determine the concentration of iso-octane produced from catalytic cracking of rubber seeds oil, Gas-liquid chromatography (GC) is used since it is a sufficient method to analyze the cracked fatty acid. Simultaneously, GC also determines certain chemical component in complex mixtures in the cracked fatty acid, with isooctane as desired component. When isooctane is detected in the cracked fatty acid, it shows that the fatty acid can be converted and continuously produced as biopetrol.

1.4 Problem Statements

Fossil fuels which are derived from natural resources such as anaerobic decomposition of buried dead organisms have been already known to have unsecured energy consumption. It was also finite and indeed will only suffice for a few generations. A new alternative is necessary to sustain the world energy consumption for the future.

In addition, Malaysia has around 1.2 million hectare plantation of rubber tree and the seed from rubbers tree can be found in an abundant since its is non-edible. However, these this rubber seeds are not utilized as its latex. Nonetheless, the seeds remain underutilized although oil produced has the potential to be used in a number of applications. Rubber seed oil has properties that qualify it to be used in biopetrol. Production of biopetrol is one of potential fuel that can be used in transportation sector and it can be produced from rubber seed oil via catalytic cracking method.

Besides that, the price of fossil fuels nowadays is increasing drastically that caused many other expenses to increase. Additionally, the dependencies on foreign countries can create negative impact on economy. In Malaysia only, for example starting 1st September 2009, the retail price of RON97 petrol increased from RM1.80 per liter to RM2.00 per liter.

Considering of pollution and global warming factor where the production and consumption of fossil fuel have caused the environmental damage by increasing the carbon dioxide concentration in the atmosphere.

Furthermore, majority of vehicles used in the world and also in Malaysia are petrol-used vehicles. This factor contributes to find other alternative fuels resources to sustain the finite fossil fuel.

1.5 Research Objectives

Based on the aforementioned research background and problem statement, the objectives of this study are:

- i- To extract fatty acid from rubber seeds kernel
- ii- To synthesized isooctane from rubber seed oil through heterogeneous catalytic cracking using Kaolinite as catalyst

1.6 Research Scopes

In order to achieve the objectives stated above, the following scopes of study have been considered:

- i- Extraction of fatty acid from rubber seeds using soxhlet extraction method
- ii- Application of catalytic cracking method to crack the fatty acid complex into smaller hydrocarbon molecules.
- iii- Determination of the concentration of isooctane using chromatography method.

1.7 Rational and Significance

Biopetrol is biodegradable and made from renewable resources which are able to sustain the energy supply for transportation. Biopetrol is safe to handle and transport because it is as biodegradable as sugar, ten times less toxic than table salt, and burns at a relatively high temperature. Biopetrol actually degrades about four times faster than petroleum-based diesel fuel when accidentally released into the environment.

Biopetrol is sulfur-free fuel and able reduce the emission of green emission gas. The production and use of biodiesel creates less carbon dioxide emissions than conventional diesel fuel. Carbon dioxide is a greenhouse gas that contributes to global warming by preventing some of the sun's radiation from escaping the Earth. Burning biopetrol fuel also effectively eliminates sulfur oxide and sulfate emissions, which are major contributors to acid rain. That is because, unlike petroleum-based diesel fuel, biodiesel is free of sulfur impurities.

Rubber seeds were not edible but could be found in abundance in the country, adding that, there were 1.2 million hector of rubber plantation in Malaysia. The oil that produced from rubber seeds is not viscous and can be used in cold climates without much modification, adding that there was between 30% and 40% of oil in rubber seeds.

Fatty acid can be easily found in most vegetable oil. Fatty acids are merely carboxylic acids with long hydrocarbon chains which may be saturated or unsaturated. The hydrocarbon chain length may vary from 10 to 30 carbons (most usual is 12-18). Through catalytic cracking process, the long chain of hydrocarbon

can be cracked into smaller hydrocarbon consist of 5 to 10 carbons where 8 carbons assigned isooctane structure.

Furthermore, rubber seeds are not much in use, so the production of biopetrol wider the application of rubber seeds oil.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The fast diminishing energy reserves, greater environmental awareness and increasing energy consumption have led to an intensified search for viable alternative sources of energy globally (Shek,2007). In this respect, in recent years a great deal of attention has been directed to plant-based sources of fuels.

Biopetrol from rubber is biodegradable and non-toxic since from the environmental point of view, fuel from vegetable sources is environmentally friendly. It is able to suppress certain pollutants that come up from the exhaust, with the exception of NO_x in certain cases, where unpredictable results occurred. Biopetrol could be an answer to the future air emission control. The application of existing biodiesel from rubber seed oil in motor vehicle has been proven to be successful (A.S Ramadhas *et al.*, 2005).

Since, Malaysia is the gross producer of rubber seed from rubber tree, the production of biopetrol can reduce the economic dependence on petroleum oil, either local or foreign. In many cases this renewable energy production will be cheaper than the traditional energy supply by means of fossil fuels, at least if the viewpoints of national economy and worldwide ecology are also taken into consideration (Ramly,2001).

2.2 Biofuel

The term biofuel or biorenewable fuel (refuel) is referred to as solid, liquid or gaseous fuels that are predominantly produced from biomass (Chhetri AB *et al.*, 2008). Liquid biofuels being considered world over fall into the following categories: (a) bioalcohols (b) vegetable oils and biodiesels, and (c) biocrude and synthetic oils (Demirbas A *et al.*, 2008). Biofuels are important because they replace petroleum fuels. It is expected that the demand for biofuels will rise in the future. Biofuels are substitute fuel sources to petroleum however; some still include a small amount of petroleum in the mixture (Demirbas A *et al.*, 2008). Common forms of biofuel are bioethanol, biodiesel and biogas.

Today bioethanol is the most used non-fossil alternative engine fuel in the world. The choice of raw material depends on local conditions. Bioethanol is good alternate fuel that is produced almost entirely from food crops. An important advantage of crop-based ethanol is its greenhouse benefits (Demirbas A *et al.*, 2008).

The biggest difference between biofuels and petroleum feedstocks is oxygen content (Demirbas A,2007) Biofuels are non-polluting, locally available, accessible, sustainable and reliable fuel obtained from renewable sources (Demirbas A,2007). Sustainability of renewable energy systems must support both human and ecosystem health over the long term, goals on tolerable emissions should look well into the future (Karki S, 2008). Liquid biofuels for transportation have recently attracted huge attention in different countries all over the world because of its renewability, sustainability, common availability, regional development, rural manufacturing jobs, reduction of greenhouse gas emissions, and its biodegradability (Darmidas A,2009).

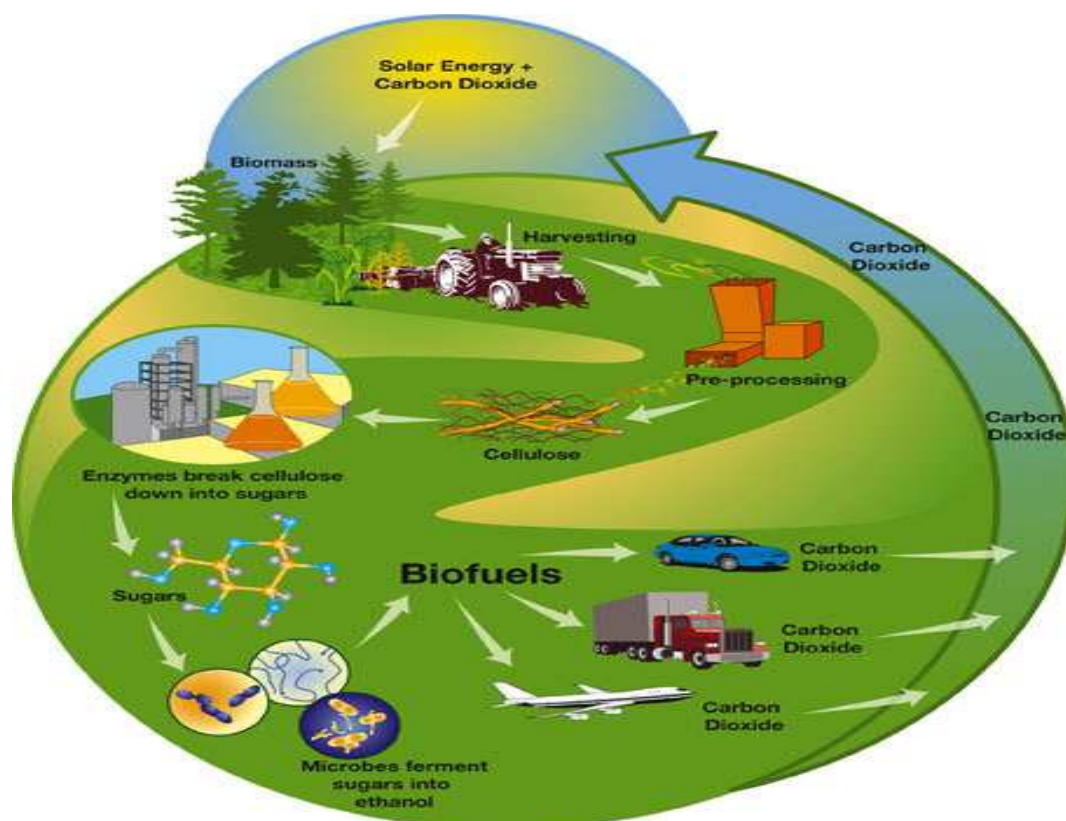


Figure 2.1: Biofuel conversion, (adapted from rayyaa.wordpress.com,2009)

2.3 Fatty Acid

By referring the World Encyclopedia (2009), a fatty acid is a carboxylic acid with a long unbranched aliphatic tail (chain), which is either saturated or unsaturated. Fatty acids are aliphatic monocarboxylic acids derived from, or contained in esterified form in, an animal or vegetable fat, oil, or wax. The hydrocarbon chain length may vary from 10-30 carbons and most usual are 12 to 18 carbons (Virtual Chembook,2003). By extension, the term is sometimes used to embrace all acyclic aliphatic carboxylic acids (International Union of Pure and Applied Chemistry,2007).

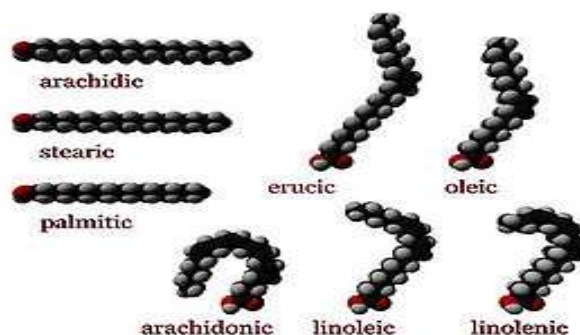


Figure 2.2: Three dimensional representations of several fatty acids (Adapted from Virtual Chembook,2003)

2.4 Rubber Seed Oil

Rubber seeds are an abundant source of non-edible oil that is available in Malaysia (Azizan, 2008). The rubber plant which is widely used as a natural source of rubber has been reported to have oil rich seeds (Njoku *et al.*, 1996). Although there are variations in the oil content of the seed from different countries, the average oil yield have been reported to be 40% (Hilditch *et al.*, 1951; Njoku *et al.*, 1996). 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 (Sthapitanonda *et al.*, 1981; Njoku *et al.*, 1996). The industrial value of a vegetable oil generally depends on its specified fatty acids and the ease with which it can be modified or combined with other chemicals (Pryde and Rothfus, 1989).

Rubber Seed Oil (RSO) contains 17–20% saturated fatty acids (myristic, palmitic, stearic, arachidic, and behenic) and 77–82% unsaturated fatty acids (palmitoleic, oleic, linoleic, linolenic and arachidoleic) (Hardjosuwito and Hoesnan, 1978; Njoku *et al.*, 1996). This study was undertaken to determine whether rubber seed oil are desirable as alternative petrol fuel.

Table 2.1: Physicochemical properties of crude and refined (bleached) rubber seed oil (O.E. Ikwaugwu *et al.*, 2000)

Analysis	Crude RSO	Refined RSO
Physical state at 30°C	Liquid	Liquid
Colour	Golden yellow	Golden yellow
Specific gravity at 30°C	0.922	0.918
Refractive index at 40°C	1.4654	1.4650
Viscosity (cSt) at 30°C	41.24	37.85
Smoke point (°C)	245	244
Flash point (°C)	294	290
Fire point (°C)	345	345
Acid value	4.0	1.0
Free fatty acid (as oleic)	2.0	0.5
Peroxide value (meq:kg)	2.5	1.0

Iodine value	142.6	142.6
Saponification value	194.0	185.8
Unsaponifiable matter	1.18	0.16

2.5 Cracking of Hydrocarbon

Cracking is the name given to breaking up large hydrocarbon molecules into smaller and more useful bits. This is achieved by using high pressures and temperatures without a catalyst, or lower temperatures and pressures in the presence of a catalyst (Behar *et al.*,1991; Kuo and Michael,1994).

There is not any single unique reaction happening in the cracker. The hydrocarbon molecules are broken up in a fairly random way to produce mixtures of smaller hydrocarbons, some of which have carbon-carbon double bonds (R. Zana *et al.*,2001). One possible reaction involving the hydrocarbon $C_{15}H_{32}$ might be:

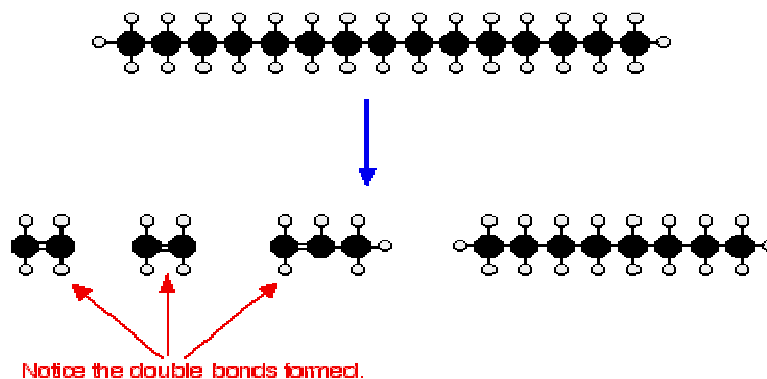
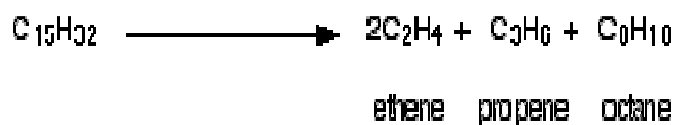


Figure 2.3: Reaction of hydrocarbon $C_{15}H_{32}$

This is only one way in which this particular molecule might break up. The ethene and propene are important materials for making plastics or producing other organic chemicals. The octane is one of the molecules found in petrol (gasoline).

2.5.1 Catalytic Cracking

Modern cracking uses zeolites as the catalyst. Besides that kaolinite also can be use as the catalyst because it consist of transition metal element such as silicon and aluminium. These are complex aluminosilicates, and are large lattices of aluminium, silicon and oxygen atoms carrying a negative charge. They are, of course, associated with positive ions such as sodium ions. The alkane is brought into contact with the catalyst at cracking temperature and moderately low pressures. (M.L. Ocelli *et al.*, 2001).

The kaolinite catalyst has sites which can remove a hydrogen from an alkane together with the two electrons which bound it to the carbon. That leaves the carbon atom with a positive charge. Ions like this are called carbonium ions (or carbocations). Reorganisation of these leads to the various products of the reaction.

2.6 Kaolinite as Catalyst

The importance of kaolinite is remarkable. As one of the most abundant mineral in soils and sediments, its properties are such that it interacts with other soil elements to contribute to the mechanical stability of the soil column (Huertas *et al.*, 1999; Chen *et al.*, 2000). Kaolinite is a 1:1 layer mineral and a product of advanced weathering processes. One layer of the mineral consists of an alumina octahedral sheet and a silica tetrahedral sheet that share a common plane of oxygen atoms and repeating layers of the mineral are hydrogen bonded together (Bear, 1965). As a consequence of this structure, the silica/oxygen and alumina/hydroxyl sheets are exposed and interact with different components in the soil (Grim, 1968). This octahedral structure increases the surface area for reaction occurs.

Frost (1998) discusses outer and the inner hydroxyl groups of the alumina hydroxyl sheet. The outer groups are situated along the unshared plane of the alumina hydroxyl sheet, while the inner groups are located along the plane that is shared with and borders on the silica oxide sheet. The movement of the inner hydroxyl plane is restricted as a result of chemical bonding between the silica and alumina sheets. Unlike smectites, kaolinite is non-expanding and as a result of its

high molecular stability, isomorphous substitution is limited or nonexistent (Mitchell, 1993). Kaolinite is the least reactive clay (Suraj *et al.*, 1998). However, its high pH dependency enhances or inhibits the adsorption of metals according to the pH of the environment (Mitchell, 1993), and this metal adsorption is usually accompanied by the release of hydrogen (H⁺) ions from the edge sites of the mineral. Adsorption may also take place on the flat exposed planes of the silica and the alumina sheets (Spark *et al.*, 1995).

Table 2.2: The properties of kaolinite (Tian-Jun Rong *et al.*, 2002)

SiO ₂ (wt.%)	46.54
Al ₂ O ₃ (wt.%)	39.54
Specific surface area (m ² g ⁻¹)	41.1
Specific surface area (calcined at 800 °C) (m ² g ⁻¹)	24.3
Retention of Specific surface area (%)	59.12
Micro-reaction activity (%)	13.4

2.7 Soxhlet Extraction Method

In its classical implementation, this was originally used to determine fat in milk (F. Soxlet, 1879). The sample is placed in a thimble holder that is gradually filled with condensed fresh extractant (term used to refer to the solvent used for extraction) from a distillation flask (see figure 3). When the liquid reaches the overflow level, a siphon aspirates the solute from the thimble-holder and unloads it back into the distillation flask, thus carrying the extracted analytes into the bulk liquid. This operation is repeated until extraction is complete. Operationally, Soxhlet extraction is thus a continuous–discrete technique. In fact, since the extractant acts stepwise, the assembly operated as a batch system; however, solvent is recirculated through the sample, so the system also operates in a continuous manner somehow.

Conventional Soxhlet extraction has some attractive advantages. Thus, the sample is repeatedly brought into contact with fresh portions of solvent, which

facilitates displacement of the transfer equilibrium. Also, the system remains at a relatively high temperature by effect of the heat applied to the distillation flask reaching the extraction cavity to some extent. In addition, no filtration is required after leaching and sample throughput can be increased by performing several simultaneous extractions in parallel, which is facilitated by the low cost of the basic equipment.

Moreover, Soxhlet extraction is a very simple methodology that requires little training and seemingly subject to no matrix effects – this assertion is not strictly true as seen when Soxhlet extraction is compared with supercritical fluid extraction of analytes strongly bound to their matrix (M.D. Luque de Castro *et al.*, 1994).

The most serious drawbacks of Soxhlet extraction as compared to other techniques for solid sample preparation are the long time required for extraction and the large amount of solvent wasted, which is not only expensive to dispose off, but also the source of additional, environmental problems (M.D. Luque de Castro and F. Priego-Capote, 2009). Samples are usually extracted at the solvent boiling point over long periods, which can result in thermal decomposition of thermolabile target species. Also, a conventional Soxhlet device provides no agitation, which would help to expedite the process. In addition, the large amounts of solvent used call for an evaporation–concentration step after extraction. Finally, the Soxhlet technique is limited by solvent and difficult to automate.

Conventional Soxhlet extraction, with its advantages and shortcomings, has been used as starting point for the development of a variety of modifications intended to alleviate or suppress the latter while keeping or even improving the former. Most of the modifications reported over the last few decades have been aimed at bringing Soxhlet closer to that of the more recent techniques for solid sample preparation, by shortening leaching times with the use of auxiliary forms of energy and automating the extraction assembly.

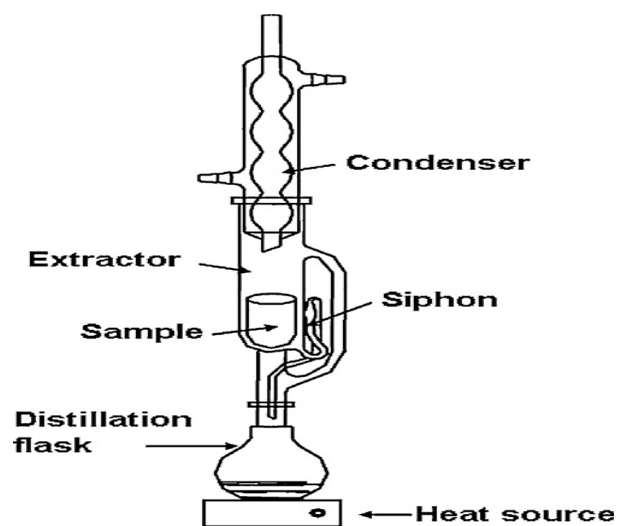


Figure 2.4: Soxhlet extractor