



Cambridge
International

Professional Research Thesis

Titled

**The use of Libyan oil raw materials in the manufacture
of industrial detergents and soap**

Researcher

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Supervisor signature

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Thanks and gifts

My dear homeland, which I sacrifice my soul and blood for, in the pursuit of its prosperity... The homeland is the love and the dream for which we live and because of which we exist... My homeland comes first and last, and nothing but my homeland deserves love... My beloved homeland, where I was born, raised, and educated on its soil, I thank you for what you have given me, and here I am, in return, presenting you with the culmination of my academic and professional journey over the past years, hoping that Almighty God grants me success for the good of myself and the nation. My success is only by the grace of Almighty God.

I extend my thanks to Rediv University and the esteemed Dr. Mohamed Said, who supervised this work, as well as all the supervising committee members. I also thank Modern Tunisian Company, especially Engineer Amina Ben Abdullah, for their efforts, and thanks to Hudhud Libya Chemicals Company for the services they provided. I thank everyone who supported me, especially my wife and children, who gave me all the comfort, encouragement, and support to bring this work to light.

SUMMARY

The soap and detergent industry is considered one of the most important industries today and is one of the pillars of the national economy. Hundreds of tons of raw materials such as sulfonic acid, fatty acids, liquid detergents, soaps, and various cleaning powders are imported. These imports are valued at millions of dollars. This industry relies on petroleum derivatives such as paraffins, cyclohexane, sulfur, and urea, which are produced at Libyan refineries in Ras Lanuf, Zawiya, Tobruk, and Mellitah.

This industry requires specific oil specifications to obtain straight-chain paraffins that can be sulfonated with sulfur produced in Mellitah factories. These paraffins can also be oxidized to obtain fatty acids, which are now widely used in soap manufacturing.

Research has begun on obtaining kerosene specifications for the production of alkylbenzene, which is used to produce the active ingredient. We relied on the specifications of global companies with extensive experience in alkylbenzene production, such as Al-Amreya Company in Egypt, some Iraqi companies, and some European companies. Contact was made with the Zawiya and Ras Lanuf refineries to obtain kerosene samples, which, according to some studies, contain good proportions of paraffins and aromatic compounds. The paraffins can be separated using Urea Adduction and methanol techniques, which are manufactured at the Ras Lanuf complex in Libya.

The study Problem.

The lack of utilization of petroleum derivatives produced by refineries, such as kerosene and aromatic hydrocarbons (from which benzene is extracted), as well as sulfur from the Mellitah company's plants, which are produced in large quantities, in the soap and detergent industry, is a significant issue.

It is worth noting that many previous studies presented at the Third Arab Conference on Soap and Detergent Manufacturing, held in Tripoli in 1989, addressed an important topic: "The use of paraffins to produce substitutes for fats and oils used in soap manufacturing." Similarly, the First Arab Symposium on Raw Materials in Soap and Detergent Manufacturing, held in Libya in 1991, discussed the topic of paraffin extraction in soap and detergent manufacturing. The biggest issue, however, is the lack of job opportunities for thousands of graduates from universities and institutes and their integration into this field, which involves the use of Libyan oil resources in soap and detergent manufacturing.

We witness the protests of many graduates who could enter this field if the necessary resources and encouragement were provided. The petrochemical industry is now considered one of the most important industries in the world, with a promising future. Especially as the world shifts towards alternatives to oil fuels, such as hydrogen and clean energy, the demand for petrochemical products, including raw materials for soap and detergents, is increasing every day, and they remain indispensable. Most importantly, Libya sits on a vast reserve of crude oil.

All these factors led us to undertake this research, hoping that the responsible authorities will consider it seriously and not disregard or neglect it.

The importance of studying:

Libya is one of the countries rich in oil and gas, exporting approximately 1.2 million barrels of crude oil daily. Crude oil is the main source of the economy, accounting for about 95% of the income.

With our experience in the soap and detergent industry, which spans more than 35 years of production, research, and development, income sources can be diversified by manufacturing the essential materials used in soap and detergent production. These materials are currently imported from abroad at the cost of billions of dollars in the form of raw materials, liquid detergents, and cleaning powders for the Libyan market. Producing these locally could also lead to exports, bringing in foreign currency and creating job opportunities for young graduates from institutes and universities.

Objectives of the study:

The aim of this study is to diversify income sources so that we are not solely dependent on selling crude oil and purchasing its derivatives from abroad. It also aims to create job opportunities for thousands of graduates from universities and institutes and involve the private sector in the field of manufacturing petroleum derivatives, which are fundamental in most industries.

Significant amounts of money are spent on importing detergents and soap in the form of raw and finished materials. Previous studies indicate that the Libyan market consumes more than 5,000 tons of detergents annually, with the active ingredient, which is the focus of our research, accounting for about 20% of this consumption.

By utilizing some of the materials we mentioned, such as cyclohexane, it can be integrated into other industries like polymer manufacturing, which has become essential in various industries such as plastics, resins, adhesives, and nylon production.

Additionally, this study aims to provide an opportunity for the private sector to enter global markets in the field of manufacturing petroleum derivatives, given that the raw materials are readily available, and to offer opportunities for engineers and technicians with extensive experience in the oil sector to work and innovate.

Utilizing the sulfur produced by the Mellitah gas plant in the sulfonation process is also a key objective.

Study hypotheses and questions.

The quality of the paraffins produced from Libyan crude oil, as indicated by this study, is one of the most important factors in manufacturing detergents, particularly due to the straight-chain carbon distribution. This quality is crucial for producing high-quality, biodegradable detergents, as it results in detergents with excellent cleaning power, high foaming ability, and high transparency in liquid detergents.

We wonder whether the paraffins produced from Libyan crude oil will become a future leader in the detergent industry, both locally and globally.

Study Approach.

1. *Obtain samples of Libyan crude oil from several oil fields and conduct analyses to determine the percentage and type of paraffinic content, which represents the carbon chain for producing the active ionic material. This analysis will be performed using a GC-FID Pevkin chromatograph.*
2. *Obtain samples of non-Libyan oil, specifically Iranian oil, and conduct analyses to determine the paraffinic content. The analysis will be performed using a GC-FID Pevkin ELMerclaru5580 chromatograph.*
3. *Compare the results of the analyses of Libyan crude oil with those of other crude oils in terms of paraffinic content, carbon distribution, and potential use in the detergent and soap industries. Compare the results of the Libyan paraffins analysis with the paraffins used at the alkylbenzene complex in Iraq. Additionally, compare the results of the Libyan paraffins analysis with the paraffins supplied to the Al-Amreya plant for alkylbenzene production.*

Compare the results of the Libyan paraffins analysis with the specifications of the straight-chain alkylbenzene used by "Shell Donbet."

Compare the results of the analyses with the specifications of "Petrolab."

Compare the results of the analyses with the specifications of "Procter & Gamble."

Compare the results with the specifications of "Arad."

The limits of the study:

Spatial boundaries: Tripoli, Libya Hudhud Libya Chemicals

Laboratory - Libya Chemicals Modern Chemicals Company, Sfax,

Tunisia University of Tripoli, Faculty of Science

Time limits: 2004-2024

Study plan.

Introductory Chapter: Theoretical Framework and Scientific Concepts

Section One.

First: Synthetic detergents are a mixture of various compounds, the primary of which is a surfactant that removes materials adhered to the surfaces of textile fibers or other surfaces to prevent them from sticking.

Surfactants: Surfactants consist of two different parts. One part is hydrophobic, typically a hydrocarbon chain of 10 to 15 carbon atoms in a straight chain, where a benzene ring may replace one carbon atom in the chain. The hydrophilic part, on the other hand, can vary, with the anionic type ending in a (SO₃) group.

Second: The first detergent was formulated in Germany during World War I (1914–1918), with the active ingredient being short-chain alkyl naphthalene sulfonate (AIKYL Naphthalene).

- Between 1920 and 1930, long-chain alcohol sulfates and sodium sulfate were introduced into detergent manufacturing, particularly alkyl aryl sulfonate.*
- In 1945, at the end of World War II, alcohol sulfates were produced as detergents.*
- By 1950–1955, the role of detergents became clearer, and new additives were introduced, such as sodium tetraphosphate and sodium tripolyphosphate.*

- *From 1955 to 1965, detergent production shifted to linking a branched chain to the benzene ring and sulfonating the resulting compound.*
- *In 1965, environmental issues arose due to the non-biodegradability of the branched chain attached to the benzene ring. This led to replacing the branched chain with a straight chain (n-paraffin), the subject of this research, due to its easier biodegradability.*

Third: *The most important active substances produced are **Anionic Surfactants**, which consist of a long chain ending in a sulfonate group (SO₃) and are typically straight-chain alkyl aryl sulfonic acids, such as:*

- *Dodecyl Benzene Sulfonic Acid*
- *Alkyl Benzene Sulfonic Acid*

*These groups are widely used in detergent manufacturing, particularly **alkyl benzene sulfonic acid** (straight chain), with the chemical formula:*

C₁₂H₂₅C₆H₄SO₃H

C₁₂H₂₅ - SO₃H

Chapter One

Section One:

First: Linear alkyl benzene (LAB) is one of the most crucial raw materials used in detergent manufacturing today. The specifications of this material significantly impact the properties and quality of the resulting detergent, whether it is liquid or powder for household and other purposes.

It is known that LAB can be produced using two well-known methods: the hydrofluoric acid method and the aluminum chloride method as a catalyst in the reaction between normal paraffin and benzene (Benzene Ring).

It is worth noting that LAB produced by these two methods is not entirely similar in terms of general specifications. The results of the sulfonation process for each case also differ, leading to variations in the sulfonated paste used in the production of different types of detergents, depending on whether it is produced using the first or second method.

The first method is the most commonly used in detergent manufacturing today, whereas the second method was prevalent until the early 1990s. Most production nowadays is done using the hydrofluoric acid method due to its numerous advantages, except for the production of liquid detergents, where straight-chain alkyl benzene produced using aluminum chloride is preferred over the hydrofluoric acid method.

Key Advantages of the First Method over the Second:

- *Higher conversion rate for producing straight-chain alkyl benzene.*
- *Good operational flexibility.*
- *More economical in terms of operational and maintenance costs.*

- *Reduced corrosion problems compared to the second method when operational conditions, concentrations, and purity of hydrofluoric acid are controlled.*
- *Higher sulfonation degree and better biodegradability of the product.*

One of the main differences between straight-chain alkyl benzene produced by the two methods is the percentage of isomer (i.e., I-paraffin). In the first method, the isomer content is around 10-20%, while in the second method, it ranges from 25-30% of the total isomers of alkyl benzene.

This significant difference in the isomer percentage has a clear impact on the specifications of the sulfonated paste used in detergent manufacturing, particularly in liquid detergents. It affects dissolution, viscosity, biodegradability, and cleaning performance of the detergent. Additionally, other specifications determine the suitability of straight-chain alkyl benzene for use in liquid detergents, powders, or both.

Control Factors Include:

- *Carbon distribution of C13-C10 in straight-chain alkyl benzene.*
- *Molecular weight of straight-chain alkyl benzene.*
- *Isomer percentage in alkyl benzene.*
- *Impurity levels.*

Second: *Before addressing the methods to control these specifications for producing straight-chain alkyl benzene using hydrofluoric acid or aluminum chloride, and the associated challenges in quality control, especially when the raw materials used in the production units are relatively distant from the design specifications, it is important to highlight*

global specifications for straight-chain alkyl benzene and their variations. These are compared with the specifications obtained from the alkyl benzene complex of the Arab Chemicals Company (Arad).

Tables (1), (2), and (3) illustrate the key specifications of straight-chain alkyl benzene from various well-known global companies, comparing them in terms of quality control of straight-chain alkyl benzene production concerning carbon distribution and its ratio. This depends on several factors, including the quality of kerosene produced from crude oil, which supplies the paraffin section, and the proportions of normal paraffins (n-paraffin) contained and their distribution.

Chapter Two: Practical Studies

The extraction of paraffins from crude oil can be performed using three methods:

- 1. UREA ADDUCTION*
- 2. Selective Vibrational Molecular Sieves*
- 3. Organic Solvent Crystallization*

We chose to work with the first method due to the availability of urea at Libyan factories.

Method:

A suitable quantity of crude oil is taken, and an equivalent amount of urea is added. The urea is added gradually while stirring until the mixture becomes thick. A catalyst (methanol) is then added, constituting 10-15% of the amount of urea, and stirring is continued for 10-12 hours.

The mixture is then filtered under vacuum and washed with hexane (50-80 ml) to remove any residual hexane. Once the hexane is removed, boiling water is added to dissolve the urea.

An aqueous sodium sulfate is then added and left for some time to dry the sample. The quantity is filtered and measured to be ready for analysis.

Since the analysis results of the extracted samples were unsatisfactory, a complete purification of the crude oil was performed to remove unwanted materials using one of the following methods:

- 1. Treatment with Propane or Acetone with Cooling**
- 2. Treatment with Concentrated Sulfuric Acid and Sodium Hydroxide Solution**
- 3. Bleaching with Bleaching Agents (Activating Fullers)**
- 4. Distillation of Crude Oil**

We chose to use concentrated sulfuric acid and performed the following steps:

- a. Add concentrated sulfuric acid (98%) in amounts ranging from 5-10% of the sample volume. Mix and separate in a separating funnel.*
- b. Add a 20% sodium hydroxide solution in the same amount as the acid, mix, and separate in the same funnel.*
- c. Wash the sample with saline water.*
- d. Completely remove the residual water to prepare the sample for further analysis.*

Conclusion.

We conclude this study with the positive results obtained from Libyan crude oil, achieving straight-chain paraffins with high proportions of n-C13, n-C12, and n-C11, the main components of the carbon chain for alkyl benzene (ALKYL BENZENE). With God's help, we will continue our research and studies to complete the second part of the detergents, which involves the sulfonation of alkyl benzene, converting it into sulfonic acid, and producing industrial detergents based on local raw materials.

Results.

From the study of the extraction of straight-chain paraffins from samples B2, B1, A2, and A1, as detailed in Tables 2 and 3, we observe paraffin content percentages of 48.37%, 42.99%, 39.21%, and 27.92%, respectively. These results are excellent, indicating that Libyan crude oil is rich in n-paraffins. Additionally, the high percentages of n-C11, n-C13, and n-C12, which are key components of the carbon chain for alkyl benzene, match the specifications of the Al-Amiriya complex for alkyl benzene production, the Alkyl Benzene complex in Iraq, Procter & Gamble, and Shell—the largest companies in the world for industrial detergent production. We also analyzed some crude oil samples from Iran, as shown in the table, which do not contain n-paraffins.

All these results indicate that Libyan crude oil can be effectively utilized in producing straight-chain alkyl benzene, a fundamental material for detergent manufacturing.

Recommendations:

Based on this study, which details the results from Libyan crude oil and the global standards for the required straight-chain paraffin content needed for alkyl benzene production—content that is not present in many other crude oils as outlined in the study—we recommend taking advantage of this and initiating a project or complex for the production of straight-chain alkyl benzene. This should include sulfonation using sulfur from Melliteh Company and conversion into sulfonic acid for industrial detergent production. By doing so, we will contribute to the growth of the national economy, provide job opportunities for thousands of graduates, utilize our local resources, and export the surplus to earn foreign currency.

The reviewer:

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