MIDDLE DISTILLATE FUELS
FROM SOME PETROLEUM FRACTIONS
(NAPHTHA)

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By
Onsy Ishak Habib Dimitry
(B. Sc.)

National Research Centre,
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MIDDLE DISTILLATE FUELS
FROM SOME PETROLEUM FRACTIONS (NAPHTHA)

Thesis Advisers:	**Approved**
Prof. F.G. Baddar	....
Prof. F.M. Ebeid	F.M. Ebeid
Dr. R.M. Habib	R. M. Habib
Dr. T.I. Rihan	T. I. Rihan

Prof. F.G. Baddar

Head of Chemistry Department

بسم الله الرحمن الرحيم

TO

MY PARENTS

WHO HAVE SACRIFICED SO MUCH

NOTE

Besides the work carried out in this thesis, the candidate has attended post graduate courses for two years in organic chemistry including the following topics:

1- Reaction Mechanisms.
2- Electronic, Infrared, Raman, N.M.R. and Mass Spectroscopy of Organic Molecules.
3- Instrumentation and Instrumental Analysis.
4- Microanalysis of Organic Compounds.
5- Organic Reactions.
6- Heterocyclic Organic Compounds.

He successfully passed an examination in these topics.

Prof. F.G. Baddar

F.G. Baddar

Head of Chemistry Department

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SUMMARY

Morgan coker gasoline is fractionated and the gasoline cut boiling between 80 and 150°C. is collected. This fraction, representing 70% of the full-range gasoline, is tested for specific gravity, refractive index, total sulphur content, average molecular weight and ASTM distillation. The gasoline fraction is examined by the hydrocarbon-type analysis, and is found to have the following composition, on a volumetric basis, total saturates 45.5%, total olefins 48.0% and total aromatics 6.5%.

Polymerization of the coker gasoline fraction for the production of hydrocarbons boiling in the middle distillates range is carried out using several acidic catalysts. The major operating variables are studied and their effects are discussed. The total polymerizate is fractionated into two cuts: cut I, has a boiling range below 150°C. and cut II, has a boiling range above 150°C. Cut II, in some experiments, is hydrogenated and the product is fractionated further into three cuts: cut II-a; 150-250°C., cut II-b; 250-360°C. and cut II-c; 360°C. to end point.

Catalytic polymerizations with the conventional acids: liquid phosphoric acid, phosphoric acid-Kieselguhr and

sulphuric acid yield total polymerizates in the range of 90.8 to 97.0% by wt. of charge. The highest yield of cut II; 30.0 wt. % of charge, is obtained with sulphuric acid catalyst. Hydrogenation of this product yields 21.3% by vol. of charge of cut II-b.

In the case of the Friedel-Crafts-type catalysts, the polymerizates are characterized by higher yields of cut II. The total polymerizate yields are in the range of 93.2 to 95.9 wt. % of charge. The maximum yields obtained of cut II are 47.4, 41.8, 35.0 and 40.0% by wt. of charge in the case of aluminium chloride, boron trifluoride dihydrate, boron trifluoride dihydrate-phosphoric acid and boron trifluoride dihydrate-sulphuric acid catalysts, respectively. However, the highest yield of cut II-b; 31.7% by vol. of charge, is obtained with boron trifluoride dihydrate catalyst. The properties of cut II-b of the several hydrogenated products are within the required standard specifications of gas oil.

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INTRODUCTION

As a result of the growth of the petroleum refining industry in Egypt during the past few years, and especially after the installation of the delayed coking unit of topped crude oil, a large surplus of coker and straight-run gasolines has resulted. On the other hand, there has been a shortage in the middle distillate fuels: kerosine, gas oil and diesel oil.

In our previous studies (1 , 2), the catalytic alkylation was investigated as a possible route for the study of the production of middle distillate fuels from the surplus of gasoline.

Rapid progress has been made in the development of polymerization processes for converting gaseous olefins from cracking units into liquid hydrocarbons suitable for use as high-octane motor and aviation fuels and for petrochemicals. However, few investigations if any, have been reported concerning polymerization for the production of middle distillate fuels.

The coker gasoline is rich with olefins. In this study, catalytic polymerization of these olefins is investigated as another possibility for the production of hydrocarbons boiling in the middle distillates range which is the main objective of this work.

The polymerization of an 80-150°C. fraction of Morgan coker gasoline (before being hydrogenated) is carried out using a wide variety of acidic catalysts. These include liquid phosphoric acid, phosphoric acid-Kieselguhr and sulphuric acid. Aluminium chloride, boron trifluoride dihydrate and its coordination compounds with phosphoric and sulphuric acids have also been examined. These catalysts are investigated under conditions which are not necessarily optimum and the effects of the major operating variables are discussed.

HISTORY OF POLYMERIZATION OF GASEOUS OLEFINS TO POLYMER GASOLINE

Polymerization of olefins has been known for nearly a century. However, it is only in the last fourty years that it has assumed importance in the petroleum industry. Interest in the polymerization of gaseous olefins came about through the use of cracking processes; first thermal and then catalytic cracking. Such processes normally produce rather large quantities of gases containing unsaturated hydrocarbons.

In the early days of thermal cracking, most of the light hydrocarbons were consumed as fuel in the refinery. As the demand increased for more and more gasoline of improved quality, it became economically attractive to utilize these unsaturated gaseous hydrocarbons in polymerization processes to produce higher boiling materials of high octane number.

The first commercial polymerization units were constructed in 1931 (3) and in 1934 (4). Both polymerization units were thermal, employing high temperature and pressure.

Later, a catalytic polymerization unit of gaseous olefins to motor fuel went on stream in 1934 using sulphuric