

**DEVELOPMENT OF NiW-ZEOLITE-BASED
CATALYSTS FOR HYDROCRACKING OF GAS OIL:
SYNTHESIS, CHARACTERIZATION, ACTIVITY AND
KINETICS STUDIES**

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UNIVERSITI SAINS MALAYSIA

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by

AHMED MUBARAK AHMED ALSOBAAI

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for the degree of
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PEMBANGUNAN MANGKIN BERASASKAN NiW-ZEOLIT UNTUK PERETAKANHIDRO MINYAK GAS: KAJIAN SINTESIS, PENCIRIAN, AKTIVITI DAN KINETIK

ABSTRAK

Satu reaktor goncang-bertekanan tinggi telah dibina untuk proses peretakanhidro bagi minyak gas dan kondisi pencampuran reaktor ini telah dikaji dalam penyelidikan ini. Peretakanhidro minyak gas telah dikaji keatas mangkin NiMo/Al₂O₃ pada suhu 300-450 °C, masa sentuh 30-120 min, nisbah berat mangkin kepada minyak gas 0-0.08 dan tekanan hidrogen 1000-3000kPa menggunakan reaktor goncang bertekanan tinggi. Nilai maksimum jumlah penukaran dan hasil bahan api sulingan adalah 59.61 dan 51.91%bt, masing-masing yang diperolehi pada suhu 450 °C, masa sentuh 90 min, nisbah mangkin kepada minyak gas 0.04 dan tekanan hidrogen 1000 kPa. Zeolit USY berasaskan NiMo, CoMo, NiW dan CoW disediakan menggunakan kaedah pengisitepuan basah. Keputusan ini menunjukkan mangkin NiW/USY memberikan jumlah penukaran dan hasil bahan api sulingan sebanyak 15.54 and 15.77wt%, masing-masing lebih tinggi daripada yang diperolehi daripada mangkin zeolit USY tanpa muatan. Mangkin NiW/USY dengan komposisi 5 %bt nikel dan 23 %bt tungsten memberikan jumlah penukaran dan hasil bahan api sulingan sebanyak 63.35 and 52.35 %bt, masing-masing. Suatu siri mangkin yang NiW berasaskan MCM-48 berliang meso dengan nisbah SiO₂/Al₂O₃ yang berbeza disediakan untuk mengkaji kesan kandungan alumina keatas sifat-sifat asid mangkin yang telah disintesis. Keputusan menunjukkan keaktifan dan sifat-sifat mangkin dapat diperbaiki dengan meningkatkan kandungan alumina dimana nilai maksima jumlah penukaran dan hasil bahan api sulingan yang

diperolehi pada nisbah berat $\text{SiO}_2/\text{Al}_2\text{O}_3$ 50. Bahan komposit MCM-48-USY juga disediakan dengan menyalut zeolit USY dengan satu lapisan bahan MCM-48 berliang meso pada nisbah SiO_2/USY yang berbeza digunakan sebagai penyokong untuk mangkin nikel dan tungsten. Keputusan menunjukkan nilai maksimum jumlah penukaran dan hasil bahan api sulingan adalah pada nisbah SiO_2/USY 0.5. Keputusan daripada tindakbalas peretakanhidro minyak gas menggunakan mangkin MCM-48-USY dibandingkan dengan keputusan yang diperolehi menggunakan mangkin USY dan MCM-48 yang digabungkan secara fizikal. Kinetik tindakbalas minyak gas menggunakan mangkin NiW/M50 juga dikaji. Mangkin-mangkin yang dipilih berasaskan keaktifan tindakbalas peretakanhidro, keasidan dan luas permukaan mangkin yang tinggi dengan purata saiz liang pada julat berliang meso yang amat bersesuaian untuk tindakbalas peretakanhidro minyak berat. Statistik rekabentuk ujikaji, (DOE), digunakan untuk memperolehi keadaan pengendalian optimum. Keputusan menunjukkan keadaan pengendalian optimum untuk peretakanhidro minyak gas oleh mangkin NiW/MCM-48 adalah pada suhu tindakbalas $465\text{ }^\circ\text{C}$, masa sentuh 30 min dan nisbah mangkin kepada minyak gas 0.05. Model kinetik “6-gumpal” yang mengandungi dua belas parameter kinetik telah dicadangkan untuk menerangkan tindakbalas peretakanhidro minyak gas. Keputusan juga menunjukkan hasil yang diperolehi dengan kaedah DOE adalah bersetuju dengan ujikaji yang dijalankan.

DEVELOPMENT OF NiW-ZEOLITE-BASED CATALYSTS FOR HYDROCRACKING OF GAS OIL: SYNTHESIS, CHARACTERIZATION, ACTIVITY AND KINETICS STUDIES

ABSTRACT

A high-pressure shaking reactor was fabricated for hydrocracking of gas oil and the mixing condition of this reactor was verified. The hydrocracking of gas oil was studied over NiMo/Al₂O₃ catalyst at reaction temperature of 300-450 °C, contact time 30-120 min, catalyst to gas oil ratio 0-0.08 and hydrogen pressure 1000-3000 kPa using high-pressure shaking reactor. Maximum values of total conversion and distillate fuels of 59.61 and 51.91 wt%, respectively, were obtained at temperature of 450 °C, 90 min contact time, 0.04 catalyst to gas oil ratio and 1000 kPa hydrogen pressure. USY zeolite supported NiMo, CoMo, NiW and CoW were prepared using the incipient wetness method. Over NiW/USY catalyst, the total conversion and distillate fuels were 15.54 and 15.77 wt%, respectively higher than those obtained over unloaded USY zeolite. Then NiW/USY catalyst with different nickel and tungsten loadings were prepared. It was observed that at tungsten and nickel loadings of 23 and 5 wt%, the total conversion and yield of total distillate fuels were 63.35 and 52.35 wt%, respectively. A series of NiW supported on mesoporous MCM-48 with different SiO₂/Al₂O₃ ratios was prepared to study the effect of alumina on the acidic properties of synthesized catalysts. The catalyst activity and properties were improved with increasing alumina content and found that maximum values of total conversion and distillate fuels were obtained at SiO₂/Al₂O₃ ratio of 50. MCM-48-USY composite materials were also prepared by coating USY zeolite by a layer of MCM-48 mesoporous material at different SiO₂/USY ratios and

used as support for nickel and tungsten catalysts. The maximum values of total conversion and distillate fuels were obtained at SiO₂/USY ratio of 0.5. The obtained results from hydrocracking of gas oil over composite MCM-48-USY catalysts were compared with those obtained over physically mixed USY and MCM-48 catalysts. The kinetic of gas oil was studied over NiW/M50 catalyst. This catalyst was chosen due to its high hydrocracking activity, acidity and surface area with average pore size in mesoporous range which is desirable for hydrocracking of heavy oil. Statistical design of experiment, (DOE), was used to obtain the optimum operating conditions. It was found that the optimum operating conditions for hydrocracking of gas oil over prepared NiW/MCM-48 catalyst are: reaction temperature of 465 °C, contact time of 30 min and catalyst to gas oil ratio of 0.05. A six-lump kinetic model contained twelve kinetic parameters was proposed to describe the hydrocracking of gas oil. It was found that the obtained results were in good agreement with those obtained from DOE and experimental results.

CHAPTER ONE

INTRODUCTION

1.1 WORLD ENERGY DEMAND

Energy is the vital basis of the development of human society, and is associated with several aspects of the social activities and daily life. With increasing world population and rising living standards, the demand for energy is steadily increasing in the world. As energy is an important resource, its cheap and stable supply is necessary to safeguard the economy and social development. Developing countries face the double pressure of economic growth and environmental protection as they enter the 21st century. Petroleum became more and more important to the world's economy, so important that today, without a steady flow of oil, most human activities on this planet would grind to a halt. Petroleum provides fuels and lubricants for our trucks, trains, airplanes, automobiles and precursors for the world's petrochemical industries. The fuels that are derived from petroleum supply more than half of the world's total supply of energy. Gasoline, kerosene, and diesel oil provide fuel for automobiles, tractors, trucks, aircraft, and ships.

At the end of 2006, the world was consuming 84.8 million barrels of oil per day. Global petroleum demand is expected to rise by 1.5 million barrels per day in 2007, an increase of 0.7 million barrels per day above the 2006 growth (Energy Information Administration (EIA), 2007). The world production of petroleum has been stagnant for the past few years because of the lack of new sites found. Even though there are reports that few new sites has been found to contain petroleum, the world production of petroleum is insufficient to meet the demand. In many parts of the world, light oil production is declining and heavy oil conversion, therefore, becomes increasingly important to maintain economic viability of these regions. In 2006, the price of crude oil has averaged US \$ 66.02 per barrel in the international market (Energy Information Administration (EIA), 2007). The majority of machines and equipments being made at present are designed to run using liquid fuel. For all these reasons and others, it is important to extract much useful products from crude oil. The ongoing trends in the petroleum refining industry have resulted in the need to upgrade heavy oils that otherwise are difficult to transport and market due to their high viscosity and high levels of contaminants such as sulphur metals sphaltenes carbon residues and solid particles. These have made the conversion of heavy petroleum fraction into valuable liquids products to be one of the most important objectives for upgrading heavy petroleum oils (Yang *et al.*, 1998).

1.2 HYDROCRACKING PROCESS

The conversion of heavy petroleum fraction into valuable products has been achieved mainly by thermal cracking, catalytic cracking and hydrocracking (Yang *et al.*, 1998). In thermal cracking process, hydrocarbons with higher molecular weight in heavy oils can be transformed to lighter hydrocarbon products by thermolysis at a higher temperature, which is accompanied with the formation of coke. The development of thermal cracking process for producing middle distillates has been limited because large amounts of gas and naphtha with lower quality are produced due to over cracking. Catalytic cracking is different from thermal cracking because carbon-carbon bond cleavage of hydrocarbons in the former occurs on a solid acid catalyst. However, the absence of a high partial pressure of hydrogen in the catalytic cracking process not only makes possible the rapid build up of coke on the catalyst but also results in products containing a significant amount of olefinic and aromatic compounds. Hydrocracking process using a metal supported solid acid catalyst is considered to be a fine method for producing high quality motor fuels. Hydrocracking reactions proceed through a bifunctional mechanism. A bifunctional mechanism is one that requires two distinct types of catalytic sites to catalyze separate steps in the reaction sequence. These two functions are the acid function, which provide for the cracking and isomerization and the metal function, which provide for the olefin formation and hydrogenation (Yang *et al.*, 1998).

Many catalysts used for the hydrocracking process are formed by composting various transition metals with the solid support such as alumina, silica, alumina-silica, magnesia and zeolites. Most of the conventional hydrocracking catalysts are dual functional catalysts. They have a hydrogenation–dehydrogenation function as well as an acidic function. The cracking activity is controlled mainly by the support that is acidic in nature, whereas the hydrogenation–dehydrogenation catalyst activity is due to the metals loaded on the support. High acidity tends to cause coking, which leads to deactivation. In order to prepare a suitable hydrocracking catalyst, a good balance between the two functions has to be maintained.

Zeolites and related crystalline molecular sieves are widely used as catalysts in the industry since they possess catalytically active sites as well as uniformly sized and shaped micropores that allow for their use as shaped selective catalysts in oil refining, petrochemistry and organic synthesis. However, due to the pore size constraints, the unique catalytic properties of zeolites are limited to reactant molecules having kinetic diameters below 10 Å (Maesen *et al.*, 2004). Zeolites have been successful because of their crystallinity, high surface area, adsorption capacity, and uniform size distribution which enable shape selectivity (Weitkamp, 2000).

Recently, a group of researchers at Mobil Oil Company reported a series of mesoporous molecular sieves, named M41S materials. These molecular sieves with mesopore diameters of 15-100 Å overcome the limitation of microporous zeolites and allow the diffusion of larger molecules. The most

popular members of this family are MCM-41 and MCM-48. Compared to the more familiar MCM-41, MCM-48 provides easier access to guest molecules due to its 3-dimensional pore network. This decreases diffusion limitations and make MCM-48 more resistant to pore blocking (Sun and Coppert, 2002). MCM-48 contains uniform mesopores, which are larger than nanopores and smaller than macropores, which makes the material particularly suited to reactions involving large molecules, such as gas oil. Despite this advantage over MCM-41, the synthesis of high quality MCM-48 with controlled pore size is more challenging. The synthesis of aluminium containing mesoporous MCM-48 with improved acidic characteristics is important in many catalytic applications. To improve the acidic characteristics of MCM-48, the alumina content ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio) incorporated into framework was investigated in this work. While increasing alumina content increases the activity of the catalyst, the lack of order resulting from silicate substitutions causes structure thermal instability. It is therefore important to optimize the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio to achieve a reactive and stable catalyst.

The selection of a proper catalyst for a given high activity is a complex problem. While microporous zeolites such as Y, ZSM-5 and β are playing important roles in modern petrochemical industry for their abundant uniform microporous structures and strong intrinsic acidities, much attention is being given to the development of mesoporous zeolites that provide larger pores (>2 nm) to allow the conversion of large molecules and thus overcome the limitations of microporous zeolites. At present, a popular resolvent is to prepare a composite zeolites material comprising of both the microporous zeolites

matrix and mesoporous material by multi-step crystallization. However, all of these methods mainly aim at modifying mesoporous material on its structure stability and acidity, which are still far away from microporous zeolites (Chen *et al.*, 2006). Despite the intensive research on synthesis, characterization and application of MCM-41 materials, MCM-48, being the cubic member of the M41S family, has received much less attention especially in the field of catalysis. A contraction of the unit cell occurred by substituting the silicon with larger aluminum atoms. The mesoporous molecular sieves MCM-48 possesses bi-continuous and three dimensional pore channels. Consequently, both the diffusional limitation and the pore blockage are reduced as compared to MCM-41. These characteristic properties show its potential applications in catalysis, adsorption and separation (Chang and Ko, 2004).

The main goal of this work was to develop zeolite-based catalysts with proper mesoporosity that are favourable for the hydrocracking of gas oil. For this purpose, different types of microporous, mesoporous and composite zeolite catalysts were prepared, characterized and tested for hydrocracking of gas oil.

1.3 OBJECTIVES OF THE RESEARCH

The main objectives of this study are:

- 1- To design, fabricate and verify the mixing condition of a high-pressure shaking reactor for hydrocracking of gas oil.
- 2- To study the effects of various operating conditions (temperature, time, hydrogen pressure and catalyst to gas oil ratio) in the hydrocracking of gas oil over commercial NiMo/Al₂O₃ catalyst.
- 3- To synthesize and characterize a series of transition metals NiMo, NiW, CoMo and CoW with different active component and promoter loadings supported on USY zeolites and test the activity of these catalysts for hydrocracking of gas oil.
- 4- To prepare and characterize a series of NiW supported on various types of prepared MCM-48 and USY/MCM-48 and test the activity of these catalysts for hydrocracking of gas oil.
- 5- To obtain the optimum operating conditions for hydrocracking of gas oil over NiW/MCM-48 catalyst using design of experiment (DOE).
- 6- To develop the kinetic model for hydrocracking of gas oil over NiW/MCM-48 catalyst that included six lumps, namely, gas oil, gasoline, kerosene, diesel, gas (C₁-C₅) and coke with six cracking reactions and to determine the kinetic parameters.

1.4 SCOPE OF WORK

High-pressure shaking reactor was designed and fabricated to study the hydrocracking reaction of gas oil under industrially relevant conditions with an excellent mixing. Firstly, hydrocracking of gas oil over commercial NiMo/Al₂O₃ catalyst was conducted in order to verify the mixing condition of the shaking reactor and find the range of operating conditions.

The influence of the acidity on the hydrocracking performance has been examined with USY zeolite as support for NiMo, CoMo, NiW and CoW catalysts. Furthermore, catalysts with different active component and promoter concentrations were synthesized to carry out the effect of active component and promoter content. Activity of catalysts were investigated in hydrocracking of gas oil at reaction temperature of 450 °C, contact time of 90 min, catalyst to gas oil ratio of 0.04 and hydrogen pressure of 1000 kPa. These operating conditions were selected according to the results obtained over commercial NiMo/Al₂O₃ catalyst.

For the hydrocracking of gas oil, large pore size is preferred to allow the conversion of large molecules and thus overcome the limitations of microporous zeolites. MCM-48 was prepared, characterized and tested for hydrocracking of gas oil. Due to the low acidity of MCM-48 materials (compared to the USY zeolite), alumina incorporated into framework to improve the acidic characteristics of MCM-48. While increasing alumina content increases the activity of the catalyst, the lack of order resulting from silicate substitutions

causes structure thermal instability. It is therefore important to optimise the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio to achieve a reactive and stable catalyst.

While microporous zeolites such as USY are playing important roles in modern petrochemical industry for their abundant uniform microporous structures and strong intrinsic acidities, and mesoporous zeolites that provide larger pores (>2 nm) to allow the conversion of large molecules and thus overcome the limitations of microporous zeolites, preparation of composite zeolites material comprising of both the microporous zeolites matrix and mesoporous material is more important. For this purpose, USY zeolite was coated with a layer of MCM-48 mesoporous material at different meso/microporous ratios. These composite MCM-48/USY materials were characterized and tested for hydrocracking of gas oil at reaction temperature of 450 °C, contact time of 90 min and catalyst to gas oil ratio of 0.04. The obtained results from hydrocracking of gas oil over composite MCM-48/USY catalysts were compared with those obtained over physically mixed USY and MCM-48 catalysts.

All prepared catalysts were regenerated and re-used for hydrocracking of gas oil. The performance of fresh and regenerated catalysts was compared to select the best catalyst in order to use it in modelling and kinetics studies.

NiW/MCM-48 catalyst was chosen due to its high hydrocracking activity and used to evaluate the effects of important variables in the hydrocracking of gas using design of experiment (DOE). Finally, kinetics study was carried out

over NiW/MCM-48 catalyst using lump parameter model based on parallel reaction of gas oil hydrocracking in order to predict all reaction parameters of gas oil hydrocracking.

1.5 ORGANIZATION OF THE THESIS

Addition to this chapter (chapter one) there are six chapters in this thesis, and each chapter gives valuable information of the thesis. Chapter two presents a review of literature. It is divided into three sections, the first section presents a general background on gas oil and its chemical composition, the second section gives details aspects of hydrocracking catalysts and process, and the last section gives a discussion of statistical analysis and reaction kinetics.

Chapter three deals with experimental methodology and focuses on the various methods used in this study. This chapter describes the materials and the experimental apparatus used in this work. The apparatus comprised four parts, i.e. the catalyst preparation, the hydrocracking system, product analysis and characterization of catalysts. It describes as well the experimental procedures, design of experiment and reaction kinetic model.

Chapters four and five present the experimental results together with the discussion. Chapter four is divided into seven sections; the first section gives general introduction on this chapter, the second section presents the preliminary results on the hydrocracking of gas oil, the third to fifth sections give results and discussions of hydrocracking of gas oil using NiW catalysts

supported on USY zeolites, MCM-48 and MCM-48/USY composite, respectively. Section six presents regeneration of catalysts.

Chapter five details on statistical design of experiment, selection of operating conditions and kinetics studies. Chapter six gives conclusions of this work. Finally, Chapter seven gives recommendations for future studies.

CHAPTER TWO

LITERATURE SURVEY

2.1 PETROLEUM

Petroleum (also called crude oil) is perhaps one of the most important substances consumed in modern society. It provides not only raw materials for the plastics and other products but also fuel for energy, industry, heating, and transportation. The oil industry classifies crude oil by the location of its origin (e.g., West Texas Intermediate, Brent) and often by its relative weight (API gravity) or viscosity (light, intermediate or heavy). Refiners may also refer to it as "sweet," which means it contains relatively little sulphur, or as "sour," which means it contains substantial amounts of sulphur and requires more refining in order to meet current product specifications. The word petroleum, derived from the Latin *petra* and *oleum*, means literally "rock oil" and refers to hydrocarbons that occur widely in the sedimentary rocks in the form of gases, liquids, semisolids, or solids (Speight, 2002). Petroleum is generally considered to be formed from animal and vegetable debris accumulating in sea basins or estuaries and buried there by sand and salt. The debris may have been decomposed by anaerobic bacteria under reducing conditions, so that most of

the oxygen was removed, or oil may have been distilled from the partially decayed debris by heat generated by earth movements or by depth of burial (Francis and Peters, 1980). The final result is a black viscous very complex mixture containing many different hydrocarbon compounds like paraffin, naphthene and aromatic hydrocarbons that vary in appearance and composition from one oil field to another. On average, crude oil contains about 84% carbon, 14% hydrogen, 1-3% sulphur and less than 1% each of nitrogen, oxygen, metals and salt (Alajbeg *et al.*, 2000).

Petroleum varies dramatically in colour, odour, and flow properties that reflect the diversity of its origin (Table 2.1) (Speight, 2002). The majority products of crude oil are LPG (liquid petroleum gas), gasoline, kerosene, diesel, gas oil and residues. Table 2.2 summarized product types and carbon number range (Speight, 2002). These products are separated by distillation in refinery (Gray, 1994; Speight, 1998). Distillation is the separation of crude oil in atmospheric and vacuum distillation columns into groups of hydrocarbon compounds of different boiling point ranges called fractions or cuts (Speight, 2002). Figure 2.1 shows schematic diagram of crude oil refinery distillation columns (Speight, 1998).

Table 2.1 Illustration of the Variation in Composition (Residuum Content) and Properties (Specific Gravity and API Gravity) of Petroleum (Speight, 2002)

Crude Oil	Specific Gravity	API Gravity	Residuum > 1000°F
California	0.858	33.4	23.0
Oklahoma	0.816	41.9	20.0
Pennsylvania	0.800	45.4	2.0
Texas	0.827	39.6	15.0
Bahrain	0.861	32.8	26.4
Iran	0.836	37.8	20.8
Iraq	0.844	36.2	23.8
Kuwait	0.860	33.0	31.9
Saudi Arabia	0.840	37.0	27.5
Venezuela	0.950	17.4	33.6

Table 2.2 General summary of product types and their carbon number range (Speight, 2002)

Product	Lower Carbon	Upper Carbon
Refinery gas	C1	C4
Liquefied petroleum gas	C3	C4
Naphtha	C5	C17
Gasoline	C4	C12
Kerosene/diesel fuel	C8	C18
Aviation turbine fuel	C8	C16
Gas oil	C12	>C20
Lubricating oil	>C20	-
Wax	C17	>C20
Asphalt	>C20	-
Coke	>C50	-

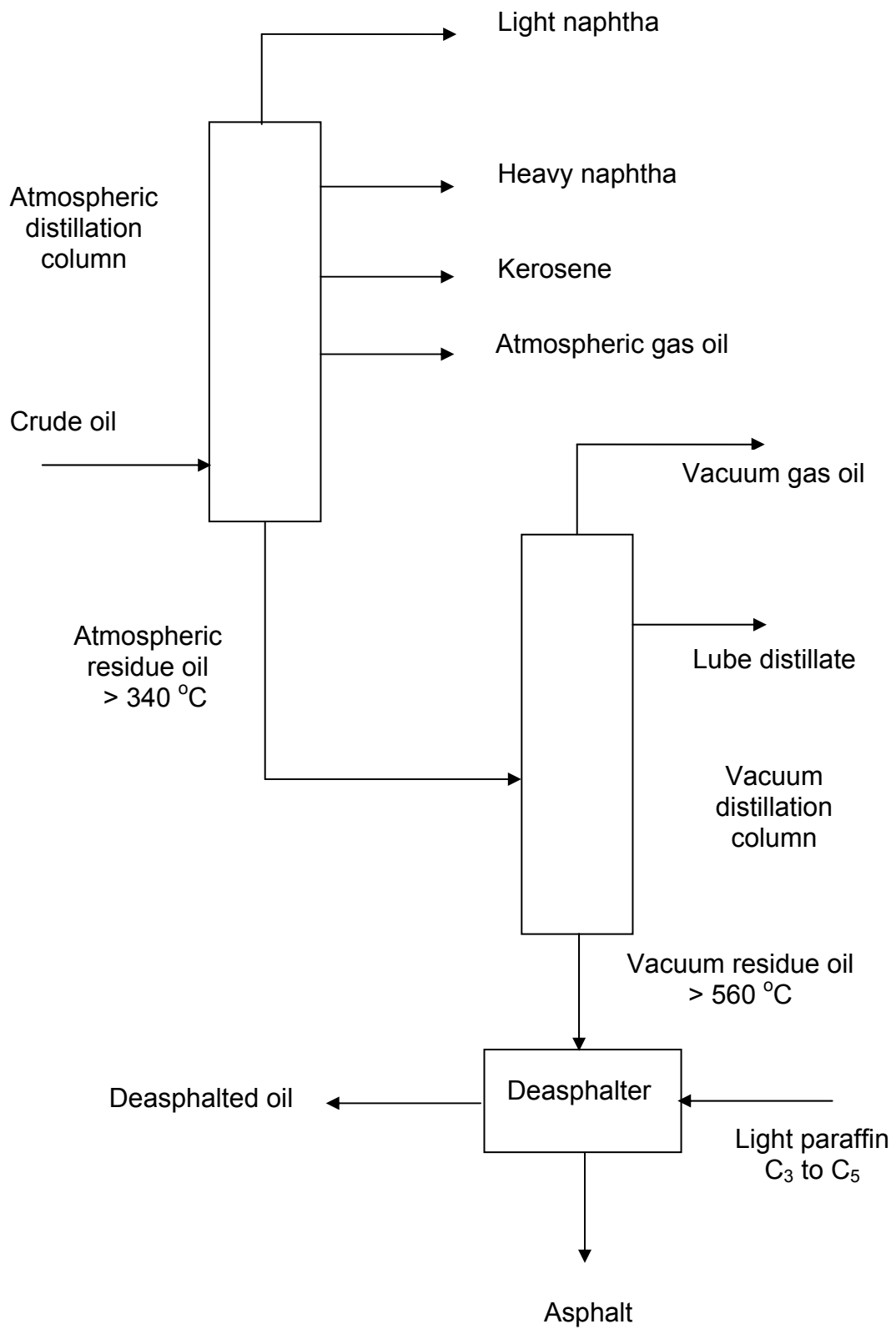


Figure 2.1 Schematic diagram of refinery distillation columns (Speight, 1998)

2.1.1 Gas oil

Gas oil is the fraction of crude oil, which is obtained by atmospheric or vacuum distillation of crude oil, and the boiling range from petroleum is between 215-337 °C (light gas oil) or 320-426 °C (heavy gas oil) (Gray, 1994). Figure 2.2 presented the boiling point and carbon number for gas oil and other petroleum products (Speight, 2002). Gas oil consists of a mixture hydrocarbon homogeneous compounds which contain carbon and hydrogen, further hydrocarbon heterogeneous compounds which contain sulphur (for example hydrogen sulphide and methyl mercaptan), nitrogen (i.e. andole and carbazole) and oxygen (i.e. methyl alcohol and acetic acid) as well as there are very small amounts of nonhydrocarbon metallic compounds as iron, copper, nickel and vanadium (Speight, 1981). Representative properties of light and heavy gas oil are shown in Table 2.3 (Gary and Handwerk, 2001).

Gas oil is also classified based on production process from crude oil by various refining processes. They have been allocated to six groups as follows (American Petroleum Institute (API), 1987):

- straight-run gas oils obtained by the atmospheric distillation of crude oil (straight-run gas oil).
- cracked gas oils obtained from refinery feedstocks by thermal, catalytic or steam cracking processes (cracked gas oil).
- hydrocracked gas oils obtained from refinery feedstocks by simultaneous processes of cracking and hydrogenation (cracked gas oil).
- gas oil distillate fuels normally obtained by blending straight-run, cracked and hydrocracked gas oils (gas oil - unspecified).

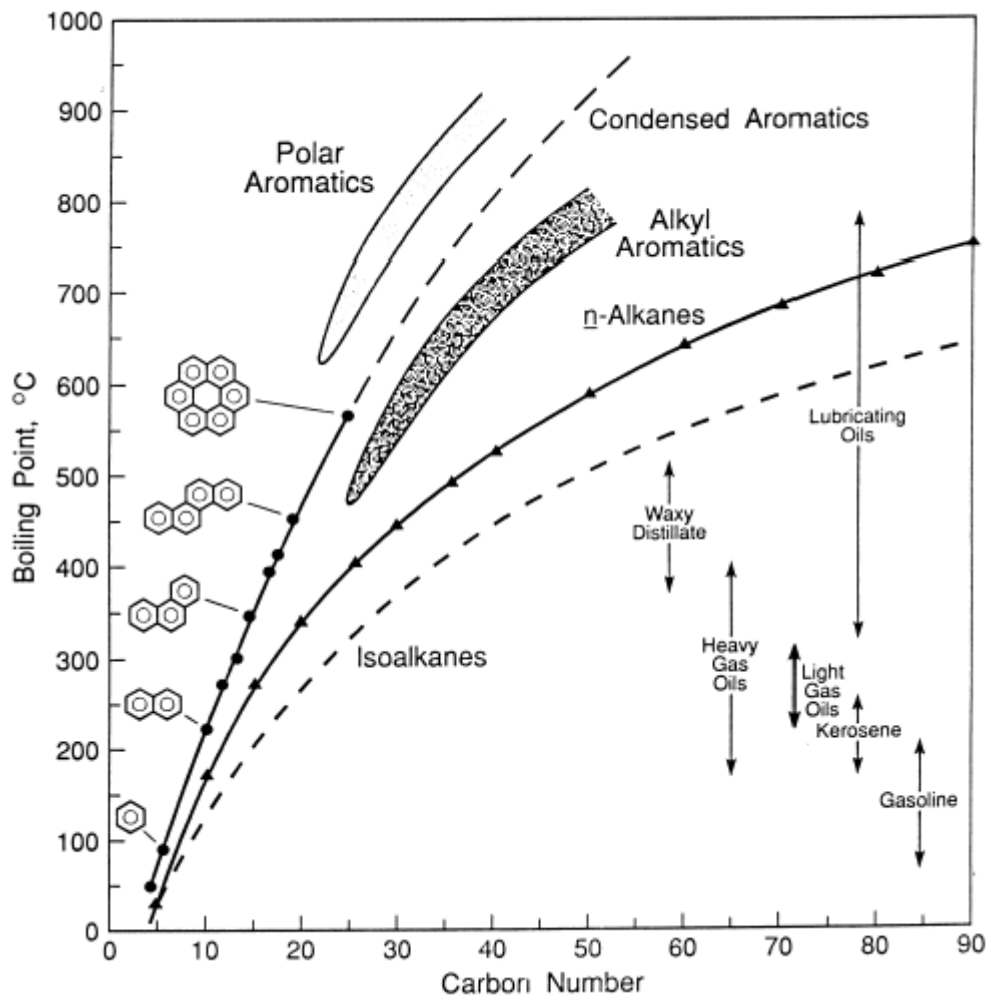


Figure 2.2 Boiling point and carbon number for gas oil and other petroleum products (Speight, 2002)

Table 2.3 Properties of light and heavy gas oil (Gary and Handwerk, 2001)

Property	Light gas oil	Heavy gas oil
Flashpoint, °C, minimum	38	38
Pour point, °C, maximum	-18	-6
Initial boiling point, °C	215	320
Final boiling point, °C	337	426
Viscosity, mm ² /s, 40 °C, minimum	1.3	1.9
Viscosity, mm ² /s, 40 °C, maximum	2.1	3.4
Density, kg/m ³ , 15 °C, (API)	850 (35)	876 (30)
Ramsbottom carbon residue, wt%	0.15	0.35
Sulphur, wt%	0.50	0.50
Water and sediment, vol%	0.05	0.05

- Distillates obtained by vacuum distillation of the residues left after the atmospheric distillation of crude oil (vacuum gas oil).
- Other gas oils obtained when straight-run or cracked gas oils are subjected to further refining processes (gas oil - unspecified).

Straight-run and vacuum gas oils typically contain 70-80% aliphatic hydrocarbons, 20-30% aromatic hydrocarbons and less than 5% of olefins. However, cracked gas oils may contain up to 75% of aromatic hydrocarbons and up to 10% olefins. Since part of the gas oils distil at temperatures in excess of 350°C, they may contain minor concentrations of 4 to 6 ring polycyclic aromatic hydrocarbons. Typical data for four gas oils, each of a different type are given in Table 2.4 (American Petroleum Institute (API), 1987).

The ever increasing demand for lighter engine fuel and higher price of light crude oil have stimulated the petroleum refining industry into looking for the possibility of processing heavy fractions as well as the comparatively cheaper heavy crude oils. Therefore, to meet the growing demand for lighter fuel the need for more efficient process is necessary. In petroleum refining, hydrocracking of heavy hydrocarbons has been carried out. Among the technologies, solid catalyzed hydrocracking processes are believed to be a promising technology because of its high product quality to produce high quality gasoline, kerosene and diesel (Ali *et al.*, 2002).

Table 2.4 Properties of four types of gas oil (American Petroleum Institute (API), 1987)

Property	Straight-run	Catalytic cracked	Hydrocracked	distillate Fuels
Aliphatic hydrocarbons, %	79.7	24	47.9	71.9
Aromatic hydrocarbons, %	20.3	72.4	21	28.1
Olefins, %	<0.1	3.7	4.4	1
Density at 15°C (g/ml)	0.82-0.85	0.972	0.837	0.834
Boiling range, °C	185-391	240-372	216-347	143-347

2.2 HYDROCRACKING OF GAS OIL

2.2.1 Hydrocracking process

Pyrolysis or thermal cracking, catalytic cracking, and hydrocracking are the three methods of hydrocarbon cracking. Thermal cracking is the breaking up of heavy oil molecules into lighter fractions by the use of high temperature without the aid of catalyst. In thermal cracking process hydrocarbons with higher molecular weight in heavy oils can be transformed to lighter hydrocarbon products by thermolysis at a higher temperature, which is accompanied with the formation of coke. The development of thermal cracking process for producing middle distillates has been limited because large amounts of gas and naphtha with lower quality are produced due to overcracking. Thermal cracking processes are commonly used to convert petroleum residue oil into distillable products, although thermal cracking processes as used in the early refineries are no longer used and the modern thermal cracking processes is visbreaking (Speight, 1998). The objective of visbreaking is to reduce the viscosity of heavy

feedstock and to increase the hydrogen-carbon atomic ratio (H/C atomic ratio). The reduction in viscosity of the unconverted residue tends to reach a limiting value with conversion, although the total product viscosity can continue to decrease (Gray, 1994). Conversion of residue in visbreaking follows first order reaction kinetics. The high viscosity of the residues is thought to be due to entanglement of the high molecular weight compounds and formation of order structures in the liquid phase. Thermal cracking at low conversion can remove side chains from the asphaltenes and break bridging aliphatic linkages. A 5-10 % conversion of atmospheric residue oil to naphtha is sufficient to reduce the entanglements and structures in the liquid phase and give at least a five fold reduction in viscosity (Speight, 1998).

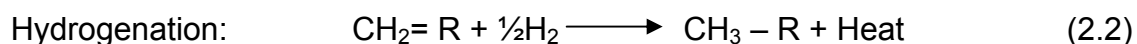
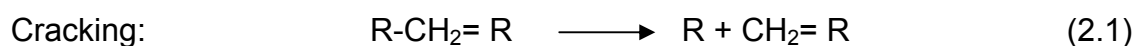
Martinez *et al.*, (1997) reported results on thermal cracking of asphaltenic residue from synthetic crude obtained by coal liquefaction. A second-order reaction was suggested for asphaltene cracking at temperature 425, 435 and 450 °C. The amount of asphaltene and yields of products, oil, gas and coke were presented as a function of residence time.

Wang and Anthony (2003) studied the thermal cracking of asphaltenes by re-examining data obtained by Martinez *et al.*, (1997). They derived the concentration and conversion or residence time relation for the yields involving the secondary cracking of oil by direct integration of the rate equations. They reported that thermal cracking of asphaltenes occurs in important heavy-oil upgrading processes such as coking and visbreaking. Their analyses confirmed that at lower temperatures the three-lump model which considered parallel

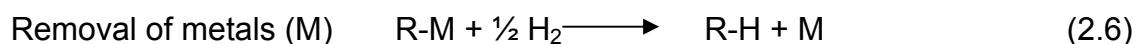
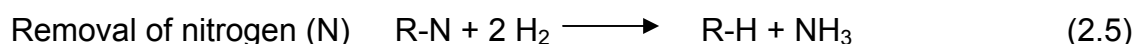
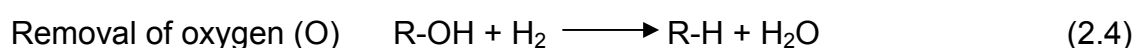
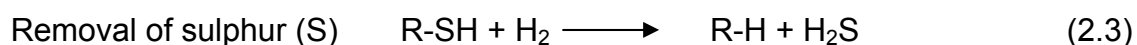
reactions of oil, gas and coke formation described the cracking behaviour whereas at higher temperature the secondary cracking of oil may be considered. This development has the potential to be useful in describing thermal-cracking processes for heavy oils.

Catalytic cracking is different from thermal cracking because carbon-carbon (C-C) bond cleavage of hydrocarbons in the former occurs on a solid acid catalyst. However, the absence of a high partial pressure of hydrogen in the catalytic cracking process not only makes possible the rapid build up of coke on the catalyst but also results in products containing a significant amount of olefinic and aromatic compounds. This not only accounts for the high-octane rating of the catalytic cracking gasoline, but also for the poor quality of middle distillates obtained in the catalytic cracking. Hydrocracking is the process of breaking up heavier hydrocarbon molecules into lighter hydrocarbon fractions by using heat and catalysts in the presence of hydrogen (Hatch and Mater, 1982). Hydrocracking process using a metal supported solid acid catalyst is considered to be a fine method for producing high-quality motor fuels. In this process, the use of higher partial pressures of hydrogen and relatively low temperatures decreases the rate of coke formation and favours the hydrogenation of olefins and aromatic compounds (Yang *et al.*, 1998). It is an endothermic reaction, provides olefins and other unsaturates for hydrogenation, while hydrogenation, an exothermic reaction, provides heat for cracking (Al-Adwani and Anthony, 1996). This process increases the yield of gasoline from crude oil. Hydrocracking is a hydrogen consuming reaction. Although hundreds of simultaneous reactions are taking place, the chemical fundamentals of this

process are well understood. It involves catalytic cracking with hydrogenation forced to prevail by extremely high hydrogen to oil ratio (≈ 1000). Catalytic cracking is the scission of a carbon-carbon single bond while hydrogenation is the addition of hydrogen to a carbon-carbon double bond (Gary and Handwerk, 1984). The role of hydrogen and temperature is very important because all hydrocracking reactions involve hydrogen contact with the reactants at a pressure above 7 MPa and temperature up to 470 °C (Speight, 1998). The feedstock is thermally cracked and hydrogenated to yield products with increased H/C atomic ratio, reduced sulphur and nitrogen content. An increase in the reaction temperature results in an increase in reaction rate but has no significant effect on the conversion. The main types of reactions that take place during hydrocracking are:



Hydrotreating:



These chemical equations are simplified since sulphur, oxygen, nitrogen and metals are present in large heteroatom cyclic compounds. Also taking place in hydrocracking processes are isomerization reactions of straight paraffinic chains to high octane isoparaffins and conversion of aromatic compounds to cycloparaffins (Laine and Trimm 1982). Hydrocracking and hydrotreating are all

first-order reactions with hydrocracking as the rate-controlling step, and kinetic data of the reaction follow a Langmuir-Hinshellwood approach (Choudhary and Saraf 1975).

Hydrocracking offers several advantages over thermal cracking such as (Gary and Handwerk, 1984):

- Higher gasoline yield.
- Better gasoline octane quality.
- Improved balance of gasoline and distillate production.
- Higher yield of isobutene in the butane fraction.

2.2.2 Hydrocracking catalysts

A Catalyst is a substance that increases the rate at which a chemical reaction approaches equilibrium without itself becoming permanently involved in the reaction. The main processes that use catalysts for petroleum heavy oil upgrading are: hydrotreating, hydrocracking and fluid catalytic cracking (FCC) (Halabi *et al.*, 1997).

Most of the conventional hydrocracking catalysts are dual functional catalysts. They have a hydrogenation–dehydrogenation function as well as an acidic function. The cracking activity is controlled mainly by the support that is acidic in nature, whereas the hydrogenation–dehydrogenation catalyst activity is due to the metals loaded on the support. High acidity tends to cause coking, which leads to deactivation. In order to prepare a suitable hydrocracking catalyst, a good balance between the two functions has to be maintained. It is