THERMODYNAMIC STUDY

OF PROPANE DEHYDROGENATION INTO PROPYLENE

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LIST OF ABBREVIATIONS

C

C_3H_8	Propane
C_3H_6	Propylene
CH_4	Methane
C_2H_4	Ethylene
C_2H_6	Ethane

F

FCCU	Fluid Catalytic Cracking Unit

H

H_2	Hydrogen

O

O_2	Oxygen
ODH	Oxidative Dehydrogenation

P

PDH   Propane Dehydrogenation

Pt   Platinum

V

VGO   Vacuum Gas Oil

LIST OF SYMBOLS

Symbol	Description	MKS Units
C_p	Specific Heat Capacity¸ Constant Pressure	J/mol.K
f_i	Fugacity¸ Pure Species I	kPa
ΔH^o	Enthalpy Change of Reaction	J/mol
ΔG^o	Gibb-Energy Change of Reaction	J/mol
g	Local Acceleration of Gravity	-
n	Number of Moles	mol
P	Absolute Pressure	atm
R	Gas Constant	J/mol.K
T	Temperature	k
y_i	Mole Fraction ¸Species i¸ Vapor Pressure	mol

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ABSTRAK

Penyahhidrogenan Propana adalah satu alternatif yang berpotensi untuk menghasilkan propolin dengan menggunakan analisis termodinamik untuk menggantikan kaedah tradisional retakan. Tujuan kajian ini adalah untuk pengagihan produk sebagai fungsi suhu yang tinggi, untuk mengenal pasti kawasan pemendapan karbon dan analisis kesan suhu keseimbangan berterusan. Penghasilan Hidrogen berbeza dengan ketara mengikut keadaan proses seperti nisbah bahan tindak balas tekanan, suhu dan suapan. Analisis termodinamik menyediakan pengetahuan penting tentang kesan pembolehubah proses penyahhidrogenan propana. Kerja-kerja sekarang bertujuan menganalisis propana penyahhidrogenan termodinamik propolin, yang meminimumkan tenaga bebas Gibbs dengan suhu sebenar dan data tekanan yang ditemui dalam penulisan. Hasil kajian menunjukkan bahawa tahap tindak balas sampingan amat bergantung kepada keadaan proses. Dengan mengira aktiviti karbon dalam sistem eksperimen, ia juga mungkin dapat menjelaskan penyimpangan antara analisis termodinamik dan keputusan eksperimen mengenai pemendapan karbon. Dari keputusan yang diperolehi di semua tindak balas yang mungkin adalah tindak balas endotermik dan suhu penyahhidrogenan perlu dinilai dalam 500 K sehingga 600 K.

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ABSTRACT

Propane dehydrogenation is a one of a promising route for producing propylene by using thermodynamic analysis to replace traditional cracking methods. The purpose of this study is to product distribution as a function over temperature, to identifying the region of the carbon deposition and to analysis the effect of temperature on the equilibrium constant. Hydrogen production varies significantly according to the operating conditions such as pressure, temperature and feed reactants ratio. The thermodynamic analysis provides important knowledge about the effects of those variables on the process of propane dehydrogenation. The present work was aimed at analyzing the thermodynamic propane dehydrogenation of propylene, using Gibbs free energy minimization with actual temperature and pressure data found in the literature. The results showed that the extent of side reactions strongly depends on the operating conditions. By computing carbon activities in experimental systems, it was also possible to explain deviations between thermodynamic analysis and experimental results regarding carbon deposition. From the results obtained¸ all of possible reactions are endothermic reaction and the dehydrogenation temperature needs to be evaluated to beyond 500 K to 600 K.

CHAPTER 1

INTRODUCTION

1.1   Background of Study

Currently, the demand for propylene in Asia is growing very fast, mainly due to the rapid increasing demand of its downstream product polypropylene. The propane dehydrogenation process, known as PDH, is used to produce high yield polymer-grade propylene through converting propane into propylene in the presence of a catalyst under high temperature, to meet the growing propylene market, independent of a steam cracker or FCC unit. It provides a dedicated, reliable source of propylene to give more control over propylene feedstock costs . Thus PDH technology has very bright future in areas rich in propane or short in propylene.

Propylene is a basic building block for the chemical industry and is used to produce a variety of products including plastics and solvents. The major source of propylene is steam cracker or fluid catalytic cracking unit (FCCU), normally as a second product. Constant growing propylene need with limited propylene supply from traditional resource has created an imbalance of supply and demand for propylene. Nowadays a shift to lighter steam cracker feed stocks with relatively lower propylene yields in certain areas has further enlarged this imbalance, thus on-purpose production methods such as propane dehydrogenation is increasing significantly.

Hydrocarbons are compound backboned by carbon and hydrogen atoms only. Typically it can be grouped into paraffinic (single C-C bond) or olefin (C=C bond) species (cf. Figure 1.1). When single-bonded hydrocarbons like propane undergoes a dehydrogenation process, propylene or propene is created. This is essentially different from cracking process whereby a long chain of hydrocarbons are split into short chains.
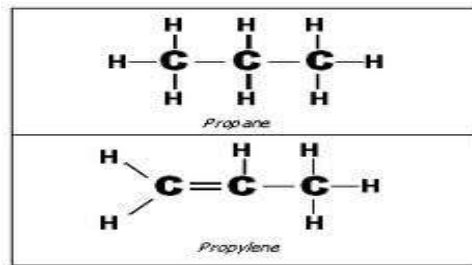
Figure 1.1 : Propane turning into propylene

In terms of molecular structure, propane is a three-carbon alkane with chemical formula of C_3H_8, normally a gas, but compressible to a transportable liquid. Propene (C_3H_6) is one of the most important substrates for chemical industry. It issued mainly for the synthesis of cumene, acrylonitrile, propylene oxide and polypropylene [1]. In industry, propene is obtained predominantly from the steamcracking of natural gas ornaphtha and from fluid catalytic cracking of liquid petroleum products. An alternative commercialized technology is the catalytic propane dehydrogenation.

Despite the apparent simplification of the reaction, propane dehydrogenation is an extremely complex process as it is a highly endothermic reaction, favoured at high temperature as it is thermodynamically limited by equilibrium at low temperatures. The major reaction in the dehydrogenation of propane is:

$$C_3H_8 \leftrightarrow C_3H_6 + H_2 \qquad \Delta H_{r,298\,K} = 129.4 \text{ kJ/mol} \qquad \text{Eqn. (1-1)}$$
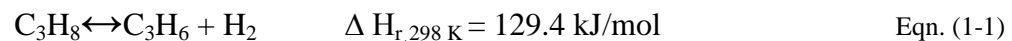
In order to obtain reasonable conversion and product yields, the reaction is normally carried out at relatively high temperature ($> 600^{\circ}\text{C}$) and low pressure. If hydrogen as reaction product is rapidly separated from the bulk fluid, the partial pressure of hydrogen will decrease and larger conversion could be attained.

Propane undergoes combustion reactions in a similar fashion to other alkanes. In the presence of excess oxygen, propane burns to form water and carbon dioxide as shown in Equation (1-2).

$$C_3H_8 + 5\ O_2 \rightarrow 3\ CO_2 + 4\ H_2O + \text{heat} \qquad \text{Eqn. (1-2)}$$

When not enough oxygen is present for complete combustion, propane burns to form water and carbon monoxide (cf Equation (1-3)).

$$2\ C_3H_8 + 7\ O_2 \rightarrow 6CO + 8\ H_2O + \text{heat} \qquad \text{Eqn. (1-3)}$$

Propane is nontoxic; however, when abused as an inhalant it poses a mild as phyxiation risk through oxygen deprivation. It must also be noted that commercial product contains hydrocarbons beyond propane, which may increase risk. Propane and its mixtures may cause mild frostbite during rapid expansion.

Propane combustion is much cleaner than gasoline, though not as clean as natural gas. The presence of C-C bonds, plus the multiple bonds of propylene and butylene, create organic exhausts besides carbon dioxide and water vapor during typical combustion.

These bonds also cause propane to burn with a visible flame. Propane is an energy-rich gas that is related to petroleum and natural gas. Propane is usually found mixed with deposits of natural gas and petroleum underground. Propane is called a fossil fuel because it was formed millions of years ago from the remains of tinysea animals and plants [3-5].

1.2   Problem Statement

Although propane dehydrogenation is a commercially well-known reaction and widely-researched in particular from catalytic and kinetic aspects, the thermodynamic perspective of this reaction has not been studied as much. Astonishingly, the search in open literature, particularly in science direct database, revealed that there are no prior publications on this topic. Furthermore, the product distributions and carbon deposition region as function of reaction temperature. Hence, this work is undertaken to enhance the thermodynamic understanding of propane dehydrogenation reaction.

1.3   Research Objective

The objective of this study is to investigate the propane dehydrogenation process into propylene via thermodynamic analysis.

1.4   Scope of the Research Work

In order to achieve the objective outlined above, the following research scopes have been identified:

1.4.1 To determine the product distribution as a function over temperature.

1.4.2 To an analysis the effect of temperature on the equilibrium constant.

1.5   Significance of the Study

There are several significant of this study that can be review from previous research paper. The most important aspect is to analyze the thermodynamic of propane dehydrogenation by using Gibbs free energy minimization method. The work provides the full thermodynamic data, useful to guide the study for propane dehydrogenation into propylene at atmospheric pressure .

This method is regarding the facility in determining carbon activities in different systems by using the simply mathematical relationship deduced in this work without the necessity of knowing the previously the chemical reactions that would lead to carbon deposition. In fact, the significant of this study is to increase the reaction of propane dehydrogenation at atmospheric pressure. This study is the most appropriate alternative that can be implementing in production of propylene .

CHAPTER 2

LITERATURE REVIEW

2.1   Introduction to Propylene

Propylene is a material intended for industrial applications, not consumer use. Propylene is a gas at normal temperature and pressure [1]. It is unlikely to be absorbed through the skin. It is not expected to persist in the environment since propylene is a gas. It is expected to go primarily into the air when released into environment. Propylene is a major industrial chemical intermediate that serves as one of the building blocks for an array of chemical and plastic products [3].

It does not cause adverse health or environmental effects at the low levels typically found in the workplace or in the environment. Propylene exposures from both natural and man-made sources are likely only in very low levels. It is flammable with a high vapor pressure; use good ventilation and avoid all ignition sources [4, 5].

2.2   The Uses of Propylene

As a major industrial chemical intermediate, propylene works as one of the building blocks for numerous chemical products such as polypropylene, cumene, isopropyl alcohol and so on. The vegetation and combustion like fire and tabacco are natural sources of propylene in the environment . Propylene with high purity production needs large separation duty. Since the boiling point of propane and propylene is very close, the column must have a lot of stages [6] .

Essentially all of the propylene produced for chemical purposes is consumed as a chemical intermediate in other chemical manufacturing processes. Commercial propylene is used to produce polypropylene, acrylonitrile, oxo chemicals, propylene oxide, cumene, isopropyl alcohol, acrylic acid and other chemicals which enable the manufacture of many chemicals and plastics [11].

Examples include: propylene glycols for paints, household detergents and automotive brake fluids, polypropylene fibers for indoor/outdoor carpeting, polyurethane systems for rigid foam insulation and flexible foam seat cushions, ABS resins for telephones and automotive trim parts molded [12]. In addition to its use as a chemical intermediate, propylene is produced and consumed in refinery operations for the production of gasoline components . Although propylene can be used as a fuel, this is not an economically attractive use.

About 56% of the worldwide production of propylene is obtained as a coproduct of ethylene manufacture, and about 33% is produced as a by-product of petroleum refining. About 7% of propylene produced worldwide is on-purpose product from the dehydrogenation of propane and metathesis of ethylene and butylenes; the remainder is from selected gas streams from coal-to-oil processes and from deep catalytic cracking of vacuum gas oil (VGO). The supply of propylene remains highly dependent on the health of the ethylene industry as well as on refinery plant economics .

In 2010, production of polypropylene represented 65% of total world propylene consumption, ranging from 53% in North America to more than 90% in Africa and the Middle East.Acrylonitrile, propylene oxide, oxo alcohols and cumene each accounted for 6–7% of global consumption.

Japan and China have the highest shares for acrylonitrile at 15% and 9%, respectively. For propylene oxide, North America and Western Europe have the largest shares at 10–12%. Oxo alcohols accounted for the highest share in Central and Eastern Europe (13%), while cumene accounts for an 8–9% share in North America, Western Europe and Japan. Following the figure 2.1, it shows world consumption of propylene in chemical application.
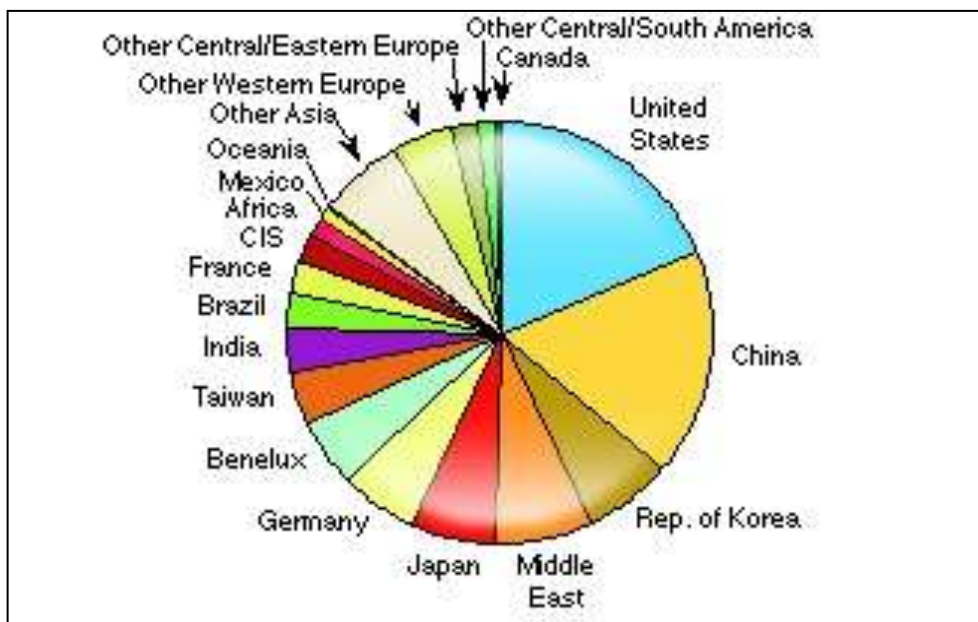

Figure 2.1 : World consumption of propylene in chemical application (2010)

From the figure below, it shows that global propylene demand grew from 37.2 million tons in 1995 to approximately 52 million tons in 2000, corresponding to an average annual growth of 5.5 percent. Demand grew at an average rate of 4.6 percent per year from 2000 to 2006 reaching almost 67 million tons .
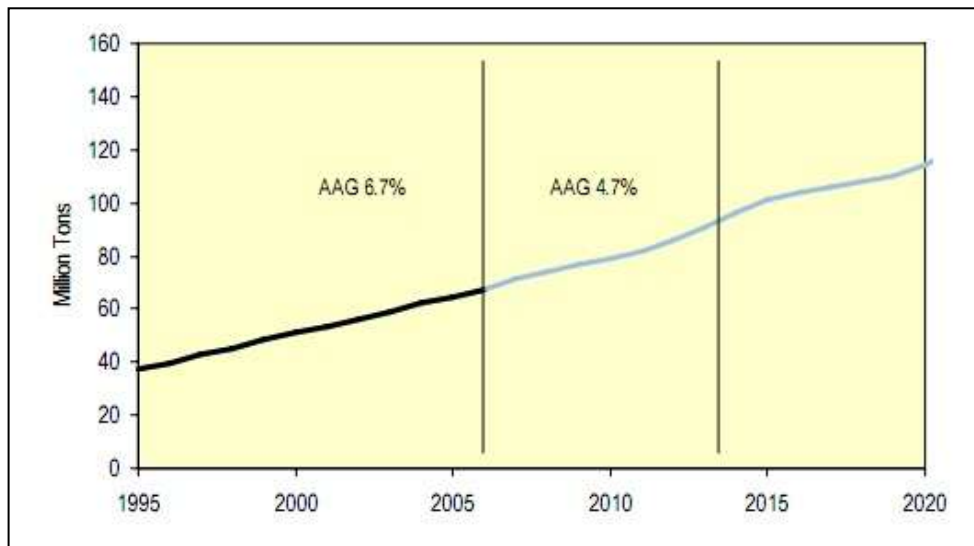

Figure 2.2: Global Propylene Demand

Demand for propylene is expected to grow at almost 5 percent annually for the period 2007-2015 to more than 100 million tons by 2015. This increase will be driven by the demand for derivatives, especially polypropylene and propylene oxide, the demand for which is growing at the rate of 5.5 percent and 4.3 percent respectively for the same period [13] . Propylene consumption by region is shown in figure 2.3.
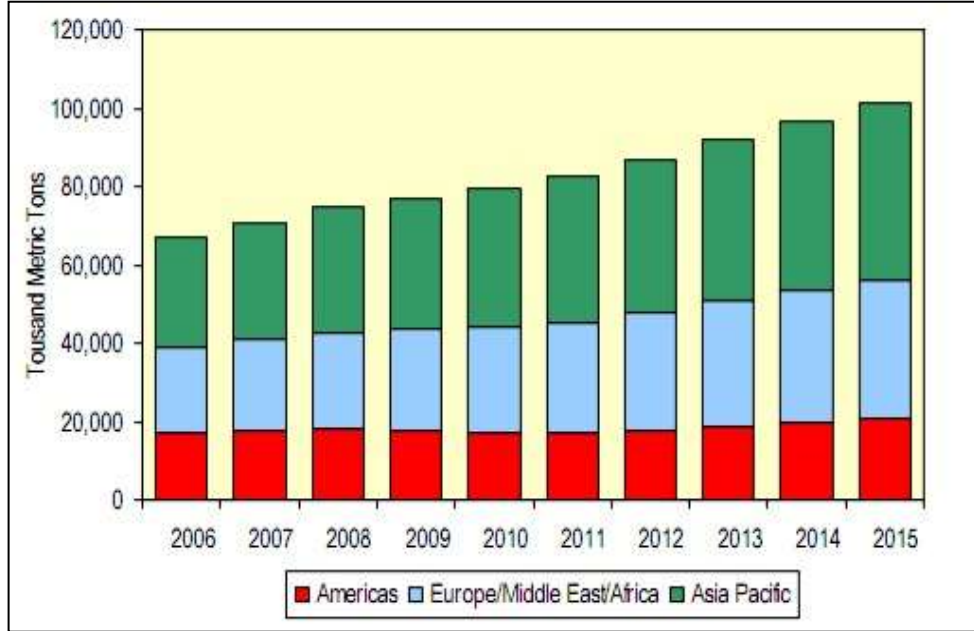
Figure 2.3 : Global Propylene Consumption Trends by Region

2.3   Propane Dehydrogenation

There has been of recent years a growing interest in the processes of propane dehydrogenation because of the rapid demand on on-purpose production of propylene .This process converts propane to polypropane with higher temperature used and low partial pressure to eventually create the dehydration reaction.The conversion rates depend on the thermodynamic limits from specific partial pressure and actual temperature used in the immediate process.

Propane dehydrogenation is a highly endothermic process. High temperatures and relatively low pressures are used to get a reasonable conversion of propane. The reaction is equilibrium limited. If hydrogen as reaction as reaction product is separated as fast as possible inside the reaction continually, the partial pressure of hydrogen will decrease and larger conversion will be achieved . To overcome the thermodynamic constraints in the commercial dehydrogenation of hydrocarbons, high temperature and low pressure conditions should be employed [15].

Thermal cracking side reactions favored by high temperatures, significantly affect the stability of propylene produced . Equilibrium conversion and reaction rate increases with the temperature, they are likewise favored at lower pressure because high reaction temperature means magnification of side reactions . This process has however several disadvantages. The dehydrogenation of propane is an endothermic process which requires relatively high temperatures and low pressures to obtain high propane conversion. The high temperature and low pressure are employed to overcome the thermodynamic constraints in the commercial dehydrogenation of propane into propylene [19].

2.3.1 Propane Dehydrogenation Analysis

As multiple reactions are involved, the equilibrium composition was more conveniently predicted via minimization of the total Gibbs energy [20]. The first phase is thermodynamics evaluation of propane dehydrogenation. The results of this evaluation is an optimum operating condition such as operating temperature at atmospheric condition and high temperature which give the highest conversion. Thermodynamic evaluation of propane dehydrogenation change due to temperature change [23]. The pressure constant and is held at atmospheric condition. The relation can be written as :

$$\frac{d(\frac{\Delta G^\circ}{RT})}{dT} = \frac{-\Delta H^\circ}{RT^2}$$
Eqn. (2-1)

Reaction equilibrium constant K correlates with temperature and Gibb's energy as described in :

$$\frac{\Delta G^\circ}{RT} = -lnK$$
Eqn. (2-2)

The change of reaction equilibrium constant affects the change of reaction conversion. The main idea of this process is to overcome thermodynamic limitations and to avoid the stage of catalyst regeneration by operating with an exothermal using molecular O_2 or air .