OPTIMIZATION OF OXIDATIVE COUPLING OF METHANE USING EXPERIMENTAL DESIGN

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This work is lovingly and respectfully in honour of my wonderful parents, Zakaria Bahari & Amalia Sumantri, my lovely wife, Mazura Jusoh and my ever delightful son, Ikhwan Firdaus.

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ABSTRACT

Direct conversion of methane, the predominant component of natural gas, to more useful chemicals and fuels has gained considerable interest. Oxidative coupling of methane (OCM), one of the various methane conversion processes, is a process for the formation of mainly ethane and ethylene. OCM has the potential of being more energy efficient compared to the energy intensive synthesis gas formation. OCM reaction using Li/MgO catalyst is optimized using the Experimental Design from 'Statsoft Statistica' version 6.0 software. The variables in this study were operating temperature, F/W and % of Li doped into the MgO catalyst while the responses were methane conversion and C_2 product selectivity. Methane and oxygen at a molar ratio of 8 were reacted at atmospheric pressure in a fixed-bed quartz reactor with F/W in the range of 2520-14620 $cm^3g^{-1}h^{-1}$ and temperature range of 592-857°C. The catalyst was loaded in the quartz reactor sandwiched between quartz wool and heated with a vertical furnace. The product gases were analyzed by an on-line gas chromatograph equipped with TCD detectors using a Porapak-N column. The Response Surface Methodology (RSM) was utilized to link one or more responses to a set of variables when firm interaction is known. Second-degree polynomial equation is chosen to link responses behaviours to change of variable level. The equation model is tested with ANOVA analysis with 99% degree confidence. The RSM contour plot gives the optimum methane conversion and C_2 selectivity of 40.7% (temperature = 778.0°C, F/W = 8978.0 $cm^3g^{-1}h^{-1}$ and % Li doped = 0.115) and 77.1% (temperature = 744.9°C, F/W = 7231.8 $cm^3g^{-1}h^{-1}$ and % Li doped = 0.095), respectively. By means of variance analysis and additional experiments, the adequacy of this model is confirmed.

ABSTRAK

Subjek penukaran terus metana, iaitu komponen utama dalam gas asli kepada bahan kimia dan bahan bakar semakin mendapat perhatian. Pengoksidaan berpasangan metana (OCM), iaitu salah satu daripada proses penukaran metana, adalah proses untuk menghasilkan etana dan etena. OCM mempunyai potensi tenaga yang lebih efisyen berbanding penggunaan tenaga yang melampau dalam proses penghasilan gas sintesis. Tujuan utama penyelidikan ini adalah untuk mengoptimisasikan tindak balas OCM dengan menggunakan mangkin Li/MgO melalui rekabentuk eksperimen daripada perisian Statsoft Statistica versi 6.0. Pemboleh ubah penting yang dipilih dalam kajian ini adalah suhu operasi, halaju dan % Li yang dimasukkan ke dalam mangkin MgO. Respon yang dipilih adalah penukaran metana dan kepemilihan C_2. Metana dan oksigen pada nisbah molar lapan bertindak balas pada tekanan atmosferik di dalam reaktor quartz dengan halaju aliran 2520-14620 $cm^3g^{-1}h^{-1}$ dan suhu 592-857°C. Mangkin dimasukkan ke dalam reactor kuartz dan diapit oleh kapas kuartz dipanaskan dalam relau menegak. Hasil eksperimen dianalisa menggunakan gas kromatografi sambung terus yang dilengkapi dengan detektor TCD yang menggunakan kolum Porapak-N. Keputusan analisis ekperimen dibuat menggunakan rekabentuk “response surface methodology” (RSM). Rekabentuk ini berjaya menghubungkan satu atau lebih respon kepada satu set pemboleh ubah apabila satu interaksi telah diketahui. Model persamaan ini telah diuji menggunakan analisis Anova dengan 99% darjah keyakinan. Berdasarkan analisa varians dan eksperimen tambahan, kejituan model disahkan. Keputusan plot kontur RSM memberikan penukaran metana dan kepemilihan C_2 sebanyak 40.7% (suhu = 778.0°C, F/W = 8978.0 $cm^3g^{-1}h^{-1}$ and % Li dimasukkan = 0.115) dan 77.1% (suhu = 744.9°C, F/W = 7231.8 $cm^3g^{-1}h^{-1}$ and % Li dimasukkan = 0.095) masing-masing. Melalui analisis varians dan eksperimen tambahan, ketepatan model disahkan.

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NOMENCLATURE

^{o}C - Degree Celsius
K - Kelvin
θ - Angle
Å - Angstron
F/W - Flow/weight
3-D - 3-Dimensional
n - Number of experiment
ΔH - Heat Enthalpy
W_m - Weight of adsorbate
P - Pressure
P_o - Saturation vapour pressure
C - BET constant
S_t - Total surface area
N - Avogadro number
A_{cs} - Molecular cross sectional area of adsorbate molecule
λ - Wavelength of X-ray
α - Extreme variable
n_o - Number of experiment at center point
Y_u - Predicted response U
Y - Response variable
β_o - Offset term/Constant
β_i - Linear term
β_{ii} - Squared term
β_{ij} - Interaction term

X_1 - Operating temperature

X_2 - F/W

X_3 - % of lithium doped

β_1 - Linear coefficient

β_2 - Linear coefficient

β_3 - Linear coefficient

β_{11} - Quadratic coefficient

β_{22} - Quadratic coefficient

β_{33} - Quadratic coefficient

β_{12} - Cross product coefficient

β_{13} - Cross product coefficient

β_{23} - Cross product coefficient

T_1 - Initial temperature

T_F - Final temperature

r_1 - Heating rate

T_d - Temperature desorbed

R_2 - Coefficient of determination

η - Mole

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CHAPTER I

INTRODUCTION

1.1 Gasoline demand and natural resources

Energy requirements in Asia Pacific countries, where economies have been expanding two to three times faster than the rest of the world, are on the rise (Haseltine, 2000). There is no doubt about the dependencies on liquid petroleum as the main energy resource. Currently, liquid petroleum is mainly used in industries and as transportation fuel. Liquid petroleum actually consumes about one-fourth of the total energy consumption. Unfortunately, oil demand soars in coming years. Petroleum reserved depleted year by year, more rapidly than they were formed, thus, creating a strong need in searching for new alternative sources (Morgan, 2000).

On a surge of economic growth, the Asia-Pasific region has been undergoing an unprecedented expansion in its use of oil products, from 11.5 million b/d in 1990, to 16 million b/d in 1995. Malaysia's indigenous proven oil reserves of 3.4 billion barrels in 2000 are significantly down from 4.1 billion barrels in 1995 (Sarmidi et. al., 2001). In

2000, Malaysia's natural gas reserves stood at about 84.2 tcf, down from 84.7tcf in 1995, but remain four times the size of oil reserves (Muller, 2001). By 2015, every Asian country will be a net oil importer, apart from Brunei. Even with limited oil consumption growth in Japan, South Korea and Taiwan, Northeast Asia will be importing 13 million b/d of oil by 2015. Whatever new fuel technologies may be in the laboratory now, the world's major institutions expect demand for oil to grow by around 40 million barrels a day (Mbd) by 2020 (Shepherd, 2001). Transport fuels are a principal factor behind the extraordinary growth in this demand, and are likely to become more important in the future as the population giants of China and India develop their economies. A general scenario is forecasted by De Jong (1996) depicting the demand of fuel throughout 1960-2020 (Figure 1.1).

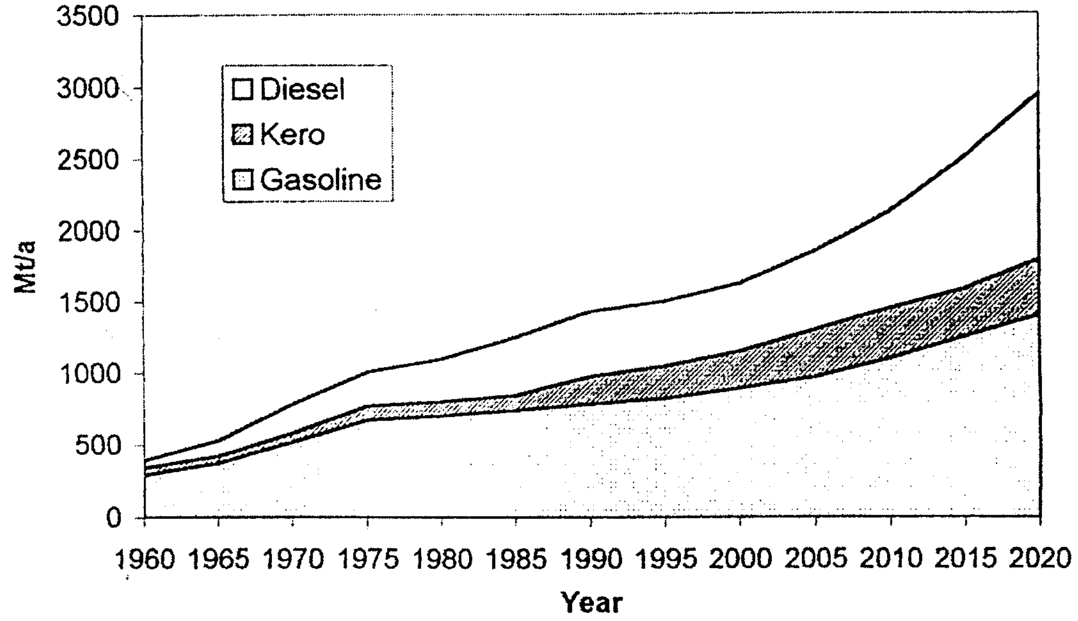

Figure 1.1: Growth in global demand of world transportation fuels (De Jong, 1996)

The oil age in South East Asia may be passing, but the gas age is well and truly on its way. Natural gas seems to be the best alternative for the replacement of petroleum. Research impetus has then been directed at the utilization of natural gas that seems to be the best alternative for the replacement of petroleum (Hutching, 1992; Lunsford, 2000; Seglin et. al., 1975). This is made possible by the development of the technology of methane conversion to higher hydrocarbons.

Methane, is currently being used for home and industrial heating as well as for the generation of electrical power. In many respects, methane is an ideal fuel for these purposes because of its availability in most populated centers, its ease of purification to remove sulfur compounds and the fact that among the hydrocarbons, it has the largest heat of combustion relative to the amount of CO_2 formed. On the other hand, methane is a greatly underutilized resource for chemicals and liquid fuels (Lunsford, 2000). Statistics, shows approximately 11% of this gas is reinjected, and unfortunately, another 4% is flared or vented (Learcher, 1999). The known reserves are enormous and rival those of liquid petroleum, as shown in Figure 1.2. Moreover, the reserves are increasing more rapidly than those of liquid petroleum, and it is anticipated that this trend will extend well into the 21st century.

Shortages of prime feedstocks for ethylene manufacture have spawned numerous attempts to use alternate raw materials. Methane is one such raw material which is the most abundant component of natural gas, usually comprising up to 90 mole % of the hydrocarbon fraction. Thus, methane represents a considerably more abundant source for ethylene than ethane or propane, the two most widely used raw materials (Bhasin, 1991) for ethylene production.

By far, majority of the research performed on the formation of higher hydrocarbons, mainly ethane and ethylene, is the oxidative coupling of methane (OCM) (Mleczko and Baerns, 1995). Interest in the direct oxidative coupling of methane has

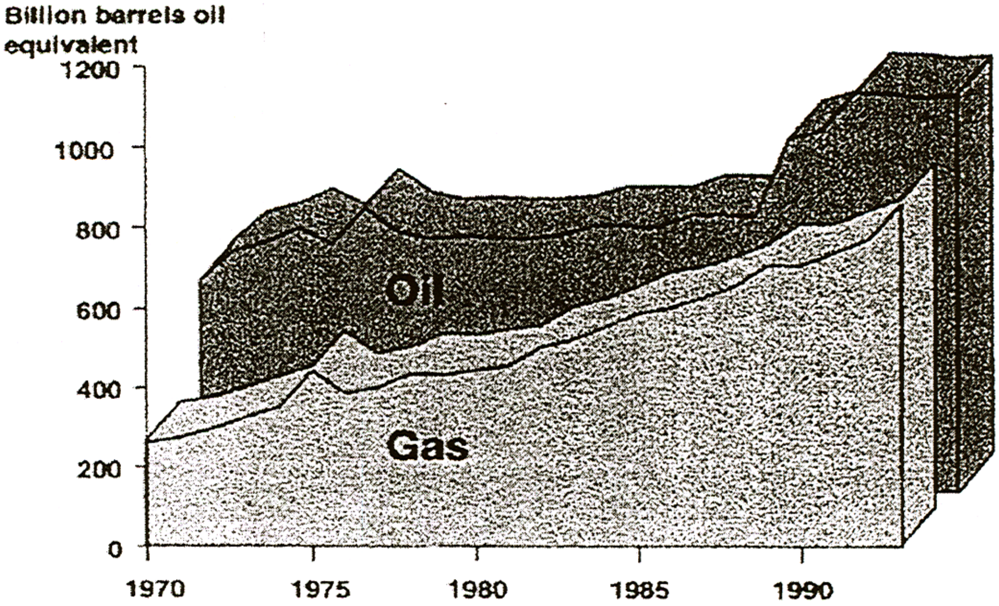

Figure 1.2: Proven world petroleum and gas reserved (Shell, 1999)

recently been heightened because of the feasibility of a potentially economically attractive route for further conversions to either gasoline, distillates or other chemicals either in a single converter or in a two-converter-in series without an intermediate separation (Bhasin, 1991). OCM is classified as direct methane conversion and has been the subject of interest as it has the potential of being more energy efficient because they bypass the energy intensive step of synthesis gas formation (Kuo, 1992).

1.2. Problem Statement and Importance of study

The literature review on the technology of methane conversion to higher hydrocarbon products has been quite extensive. For example Deboy and Hicks (1998), Conway et al. (1991), Choudhary et al. (1997), Djaidja et al. (2000) has reported their studies on OCM. Choudhary and Mamman (2000), Froment (2000) and Lange (2001) looked into Steam Reforming of Methane (SRM) while Zhu and Stephanopoulos (2001) and Lee et al. (2002) accounted for Partial Oxidation of Methane (POM). Study on CO_2 Reforming of Methane (CORM) was carried out by Teuner (2001), Amin et al. (2001) and Chin (2000). Chang (1991) and Calleja et al. (1995) have reported their studies on Fischer-Tropsch Process. In the year 2001, Anggoro (2001), Ngadi (2001), Hartog (2001) revealed their research on Gas-To-Liquid Technology whilst Lee and Foster (1996) reported their investigation on Direct Partial Oxidation (DPO) process. Unfortunately, their research still led to low conversion and selectivity and is not yet commercially viable. From this scenario, the methane conversion technology processes still needs to be improved in order to achieve commercial viability.

The ultimate challenge is how to convert the stable CH_4 to C_2^+ products with at least 30% C_2 yield. The performance of catalysts and experimental parameters such as temperature and F/W are critical in improving the methane conversion. Besides, methane conversion and C_2^+ products selectivity also depend on the catalysts. Oxidative coupling of methane is one of the vital technologies for methane conversion to C_2^+ product. Therefore, by systematically arranging the parameters according to design of experiment, an optimum result could be obtained for the OCM process.

1.3 Objective of Study:

The objective of this research is to optimize the methane conversion and C_2 selectivity in oxidative coupling of methane (OCM) using Li/MgO catalyst (various Li/Mg ratio) via Design of Experiment (DOE) from Statistica software.

1.4. Scope of Research

The research focuses on the application of metal oxide catalysts used in a plug-flow catalytic reactor. The metal oxide catalysts used in this study is Li/MgO for the oxidative coupling of methane to achieve C_2^+. Main concern in this experiment is to find out the optimum condition for obtaining a higher methane conversion and higher C_2 selectivity.

Initially, identification of vital independent variable, and their maximum and minimum values were made. The independent variables are temperature, F/W and % Li doped. Characterization of each catalytic sample will be carried out using X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Nitrogen Adsorption (NA), Temperature Programmed Desorption CO_2 (TPD-CO_2) and Fourier Transform Infrared (FTIR). Finally, catalyst testing will be performed for the oxidation of methane to C_2 using a micro packed-bed quartz reactor with 9 mm ID and 30 cm long. The experiment will be carried out according to the arrangement set by the Design of Experiment from Statistica Software. Three operating parameters in the experiment will be evaluated to reach the optimization point for the conversion of methane to ethane and ethylene. The gas products will be analyzed using an online gas chromatography equipped with porapak-N capillary column. Result analysis was carried out using response surface methodology to obtain each properties of independent variables towards methane conversion and C_2 selectivity.

1.5 Thesis Summary

In general the thesis discusses:

Chapter II elaborated the various methane conversion technologies that can be divided into two categories: indirect and direct process of methane conversion. Indirect process consists of steam reforming of methane, partial oxidation of methane, CO_2 reforming of methane, Fischer-Tropsch and, methanol to gasoline whereas direct process consists of direct partial oxidation, oxidative coupling of methane which is discussed in length and oxidative coupling of methane with CO_2. The catalysts for OCM are discussed as well as a table listing an overview of the OCM process. Characterization techniques utilized in this study was briefly elaborated and they include XRD, NA, SEM, TPD and FTIR. The design of experiment, response surface methodology (RSM), optimum condition determination and ANOVA were also discussed at the end of the chapter.

Chapter III discusses the methodology of the experiment. A research methodology flow chart attached in the beginning of the chapter provides an overview of how the research is undertaken. The preparation of catalysts and the characterization techniques (XRD, NA, SEM, TPD and FTIR) were outlined. The methods and/or specification of each characterization techniques were revealed. The experimental arrangement set by the experimental design was presented in this chapter. Operating parameters selected to be varied were temperature, F/W and % lithium doped inside the MgO catalyst. The method and specification for GC is also noted.

Chapter IV presents the results of catalyst characterization that includes XRD, NA, SEM, TPD-CO_2 and FTIR. From the results, imperative properties of the catalyst such as basicity and surface areas were known and they were consistent with results reported by other researchers.

Chapter V discusses the effect of operating parameters involved in the process. It is found that all the parameters studied influences the OCM activity in terms of methane conversion and C_2 selectivity. The C_2H_4/C_2H_6 ratio resulted from OCM process was also reported. At the end of this chapter, the blank run and catalyst ageing were discussed.

Chapter VI presents the optimization and its ANOVA analysis. The relationship between independent variables with methane conversion and C_2 selectivity can be observed from the contour plot and 3-D surface plot. The correctness of the polynomial model chosen will be proven using statistics. Via pareto chart, the most influential independent variables and their interactions can be determined. Confirmatory experimental results were included as well as the comparison of optimization results with other researchers in similar field.

Chapter VII is the conclusion and recommendation section. For conclusion, we proposed a set of operating parameters each to obtain optimum methane conversion and C_2 selectivity. Recommendations were proposed for improvement in future work and its continuation opportunities.