Conversion of Methanol to Hydrocarbons in a Supercritical Fluid Reaction Medium

by

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Abstract

This thesis work explores the effects of a supercritical fluid reaction medium on the catalytic performance of the methanol-to-hydrocarbons (MTH) reaction. The MTH reaction allows for the conversion of cheap and readily available methanol to light olefins and/or high octane gasoline. Historically, the MTH conversion has been carried out under gas phase conditions; however, under these conditions, several drawbacks have been observed which limit the useful application of this technology, including coking and heat management challenges. Supercritical fluid (SCF) reaction media have been successfully employed in other exothermic and mass transfer limited reactions, such as Fischer-Tropsch Synthesis and Higher Alcohol Synthesis, to mitigate the problems associated with traditional gas phase operation. Because of their intermediate physical properties, SCF media possess higher solvent strength and thermal conductivities than gases while also possessing gas-like diffusivities and viscosities, thus allowing for a single phase reaction environment in which both liquid products and heat are efficiently extracted from the catalyst without hindering the diffusion of gaseous reactants. To the best of the author's knowledge, this work reports the first investigation of SCF application in the MTH reaction. Isooctane was selected as the SCF medium primarily because of its low reactivity over the traditional MTH catalyst, ZSM-5. The results of this investigation suggest that, compared to operation in a gas phase environment, conducting the MTH reaction in the presence of supercritical isooctane led to improved catalyst maintenance, as evidenced in part by increased hydrocarbon production with increasing time-on-stream as well as decreased coke accumulation. Further studies are needed to better understand the effects of an SCF environment on the MTH reaction under different operating conditions which exploit the unique properties of the SCF medium and for different MTH catalytic systems.

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List of Abbreviations

DME	Dimethyl ether
FID	Flame Ionization Detector
FTS	Fischer-Tropsch Synthesis
GC	Gas Chromatography
GP	Gas Phase
HAS	Higher Alcohol Synthesis
HC	Hydrocarbon
HPLC	High Performance Liquid Chromatography
MeOH	Methanol
MFC	Mass Flow Controller
MTG	Methanol to Gasoline
MTH	Methanol to Hydrocarbons
MTO	Methanol to Olefins
RF	Response Factor
RRF	Relative Response Factor
SC	Supercritical
SCCM	Standard Cubic Centimeters
SCF	Supercritical Fluid
TCD	Thermal Conductivity Detector

TGA	Thermogravimetric Analysis
TOS	Time on Stream
WHSV	Weight Hourly Space Velocity
XRD	X-Ray Diffraction
XTL	X-to-Liquids

Chapter 1 A Review of the Methanol-to-Hydrocarbons (MTH) Reaction

1.1 Introduction

Fluctuating crude oil prices, diminishing oil reserves, and growing global energy demands have long fueled the search for viable alternatives to petroleum. According to the 2013 World Energy Outlook, from 2011 to 2035 world energy demands are projected to increase by one-third, with the contribution of petroleum to this growth decreasing from 82% to 76% and the contribution of renewables accounting for about half of the increase in electricity demands alone (IEA, 2013). Furthermore, laws have been passed which stipulate the incorporation of fuels derived from renewable resources. For example, the 2007 Energy Independence and Security Act mandates that 36 billion gallons of renewable fuels must be available for transportation use by 2022, with 21 billion gallons of this total allotted for advanced biofuels produced from cellulosic biomass (*Energy Independence and Security Act of 2007*, 2007). These advanced biofuels, such as lignocellulosic ethanol, will therefore be important in helping to supplement and eventually replace petroleum-derived fuels.

Advanced biofuels can be generated through both biochemical and thermochemical means. Thermochemical conversion pathways allow for carbon feedstocks other than crude oil to be transformed into automotive fuels and high-value chemicals by subjecting the feedstock to conditions of elevated temperature and pressure. Non-renewable carbon sources such as coal and natural gas can be gasified or reformed, respectively, to generate synthesis gas, a mixture of carbon monoxide and hydrogen. Synthesis gas, or syngas, can be subsequently upgraded to produce a variety of hydrocarbon and oxygenate species, depending on the chemical pathway chosen.

Biomass, such as switchgrass and wood chips, is organic material which is often rich in carbon and oxygen and lean in hydrogen. Like coal, biomass can be gasified to produce syngas and, subsequently, liquid drop-in biofuels and/or blending stocks. This conversion process is referred to as Biomass-to-Liquids (BTL) and is a subset of the more general thermochemical process XTL, where X stands for the type of carbon resource used. In contrast to the Bergius Process, in which coal is directly hydrogenated to liquid fuel products by slurrying coal particles with oil and iron catalyst under heat and pressure (Chang et al., 1978), XTL processes are all indirect, involving syngas generation as an intermediate step.

Regardless of the carbon feedstock used, once syngas has been generated, a variety of chemical pathways are available for subsequent upgrading of the syngas to the desired gas or liquid fractions. These pathways include Methanol Synthesis, Mixed and Higher Alcohol Synthesis, Dimethyl Ether Synthesis, Fischer-Tropsch Synthesis (FTS), and Methanol-to-Hydrocarbons (MTH). Of these pathways, only MTH is capable of producing gasoline-range hydrocarbons that have the potential for direct application in the existing US transportation infrastructure (Chang et al., 1978) as well as light olefins which serve as important feedstocks in the production of plastics and other high-value chemicals ("Honeywell's UOP And Total Petrochemicals Successfully Demonstrate Technology To Produce Plastics From Feedstocks Other Than Oil," 2010). This paper will explore the MTH pathway in greater detail and discuss one potential technique for improving the reaction performance: the use of a supercritical fluid reaction medium.

Prior to the MTH reaction, syngas produced from the thermochemical conversion of coal, natural gas or even biomass is reacted to produce methanol, which is formed from syngas with high selectivity (Spath & Dayton, 2003). This syngas-derived methanol can then be reacted over a variety of molecular sieve catalysts (e.g., zeolites) to selectively generate light olefins or gasoline-range hydrocarbons. One such catalyst is ZSM-5, a zeolite discovered by Mobil (Chang et al., 1978), whose groundbreaking investigations of methanol conversion over ZSM-5 sparked worldwide interest in the MTH pathway.

1.2 History and Commercialization of the MTH Reaction

The first recorded observation of methanol conversion to hydrocarbons was reported by W.J. Mattox in 1962. In his investigation, Mattox reacted methanol over the zeolite catalyst NaX to produce dimethyl ether (DME) and trace amounts of light olefins in the ethylene to pentene range (Chang et al., 1978). About a decade later, in the late 1970s, Mobil researchers in Princeton, New Jersey were reacting methanol with isobutene over ZSM-5 in an attempt to methylate isobutene when they unexpectedly discovered aromatics in the resulting liquid product. Reacting methanol alone over ZSM-5 resulted in complete conversion to a synthetic gasoline product consisting of olefins, paraffins, and aromatics. A litany of bench-scale studies followed, with the oil crises of the 1973 and 1978 prompting commercial-scale investigation of the Methanol-to-Gasoline (MTG) reaction (Keil, 1999).

1.2.1 Mobil Exploratory Methanol-to-Gasoline Studies

In 1980, Mobil began construction on the first commercial-scale MTG facility in New Zealand. The feedstock for the fixed-bed MTG process was crude methanol derived from syngas produced locally by the reforming of natural gas from New Zealand's Maui and Kapuni fields. By 1986, at the end of the project's startup phase, Mobil's New Zealand plant had achieved a production capacity of 570,000 tons per year of finished gasoline (Keil, 1999). The commercial plant design was largely based on a two-reactor, fixed-bed process, whose bench-scale schematic is depicted below in Figure 1.1.

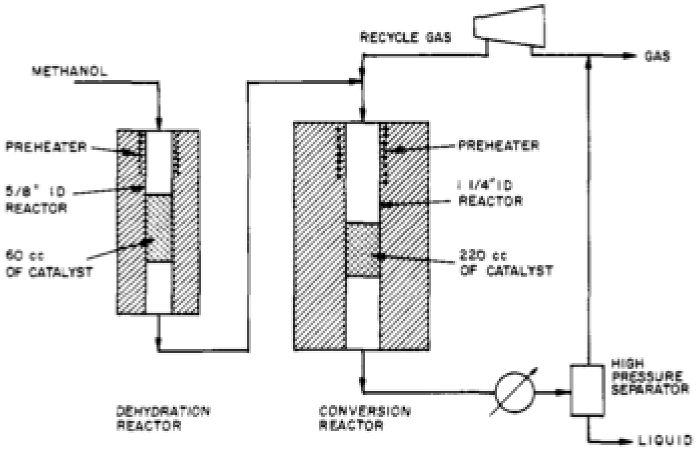

Figure 1.1 Mobil's Two-Reactor Bench-Scale Design (Chang et al., 1978)

The main purpose of the two-reactor staging shown in Figure 1.1 is to control the release of heat from the exothermic MTG reaction (Chang et al., 1978). In this process scheme, methanol is first dehydrated over an alumina catalyst at around 310-320°C inlet temperature and 26 bar to produce an equilibrium mixture of DME, water, and unreacted methanol. The dehydration reaction releases about 15-20% of the total MTG reaction heat (approximately 1.74 MJ heat produced per kg converted methanol) (Keil, 1999). The catalyst in the first reactor bed experiences very slow deactivation with time-on-stream (Chang et al., 1978).

The methanol-DME effluent from the dehydration reactor is then combined with a cooled light gas recycle and introduced into the conversion reactor, which contains Mobil's ZSM-5 catalyst. The operating conditions for this reaction are 350-370°C and 19-23 bar (Keil, 1999). Unlike the first reactor, deactivation due to catalyst coking is a major concern in the second reactor. Mobil's proposed solution for coke removal is controlled coke burn-off in air (Chang et al., 1978).

The bench-scale process reportedly ran for almost 7 days before unreacted methanol was observed in the second reactor effluent. As the reaction progressed, Mobil researchers noted several changes in the MTG product distribution with time-on-stream including an increase in gasoline-range nonaromatic hydrocarbons and a decrease in light paraffins. The gasoline obtained from the bench-scale experiments had a Research Octane Number (RON) of 94-96 and a durene (1,2,4,5-tetramethylbenzene) content of about 2.5-4.5 wt% (Chang et al., 1978). Durene is produced with high selectivity in the MTG reaction compared to other tetramethylbenzenes. Due to its high melting point (79.4°C), durene can crystallize in car engines and thus hurt vehicle performance if its concentration in gasoline exceeds about 4-5 wt% (Chang et al., 1978).

While the commercial MTG process achieved similar finished gasoline octane values (RON of around 92), the durene content was considerably lower due to the installation of a heavy gas treatment (HGT) unit specifically designed for durene removal. With the HGT unit, the final durene content of the finished commercial gasoline was only 2 wt%. However, despite the successful operation of the New Zealand plant, commercial MTG investigations ceased as the price of crude oil fell during the 1980s (Keil, 1999).

1.2.2 UOP/Hydro Methanol-to-Olefins Process

Early bench-scale experiments by Mobil researchers among others had revealed that light olefin selectivity in MTH reactions could be increased by modifying operating conditions (i.e., increasing reaction temperature and lowering reaction pressure) and by reducing catalyst acidity. However, in 1986, Union Carbide devised a fluidized-bed reaction system for converting methanol to olefins with greater than 90% selectivity using the molecular sieve catalyst SAPO-34 (Keil, 1999).

Today, the Union Carbide MTO process is survived by the UOP/Hydro MTO process, a joint project between UOP Honeywell and Norsk Hydro, which is currently operated at the demonstration-scale Total Petrochemicals facility in Belgium ("Honeywell's UOP And Total Petrochemicals Successfully Demonstrate Technology To Produce Plastics From Feedstocks Other Than Oil," 2010). The UOP/Hydro MTO process employs a fluidized-bed reactor with continuous SAPO-34 catalyst regeneration to produce a light olefin product that is 48% ethylene and 33% propylene (Keil, 1999).

1.2.3 Haldor-Topsøe TIGAS Process

Another MTG-related process currently in operation is Haldor Topsøe's Improved Gasoline Synthesis (TIGAS) process for converting 25 tons per day of woody biomass into gasoline ("Gasoline - TIGAS," 2013). Topsoe's current TIGAS project is a revival of their 1980s demonstration-scale process, which was aimed at producing gasoline from natural gas.

In the TIGAS process, the syngas, oxygenate (methanol), and gasoline synthesis steps are all operated at the same reaction pressure to reduce costs associated with high-pressure operation. Normally, the conversion of natural gas to syngas requires very high pressure (50-100 bar); however, through a combination of steam and autothermal reforming, the conversion of methane to syngas is carried out at only around 20 bar in the TIGAS process. The original TIGAS demonstration was carried out in Houston, TX for 10,000 hours before its shutdown in 1987 (Keil, 1999).

1.3 MTH Chemistry

The chemistry of the MTH reaction is largely influenced by catalyst selection and process variables such as temperature and space velocity. A variety of catalyst types have been tested under MTH conditions (i.e., temperature typically greater than 300°C, depending on catalyst structure and SiO_2/Al_2O_3 ratio (Froment, Dehertog, & A.J., 1992)), with varying results observed in terms of product distribution and catalyst stability.

1.3.1 MTH Catalysts

The types of catalysts typically used in the MTH reaction are solid-acid catalysts with well-defined pore structures which can effectively sieve reactants and products based on size and shape. These molecular sieve catalysts may be either zeolites (aluminosilicates; e.g., ZSM-5) or zeotypes such as silicoaluminophosphates (e.g., SAPO-34). Regardless of the chemical make-up of the molecular sieve, zeolites can be sub-divided into three classes based on pore size, a factor which plays an important role in determining the product distribution and deactivation characteristics of the MTH reaction (Froment et al., 1992).

1.3.1.1 Large Pore Catalysts

This class of MTH catalysts describes those with pore sizes exceeding about 6 Å in diameter. The pore channels of these catalysts may be either one-dimensional or multi-dimensional. Some examples of macroporous molecular sieves are zeolite Y and SAPO-5. Large-pore molecular sieves have been investigated in the conversion of methanol to olefins. However, the large pore size and high acidity of these catalysts renders them less selective in their product distributions, allowing for bulkier compounds such as heavy aromatics to be both formed and released from the catalyst surface. Macroporous molecular sieves, especially those with one-dimensional channels, tend to suffer from extensive coke buildup due to the greater size of their pore cavities, which permit the accumulation of coke deposits. These coke deposits can block reactive sites and clog catalyst pores (Froment et al., 1992).

1.3.1.2 Medium Pore Catalysts

Medium-pore molecular sieves have pore sizes in the 5-6 Å range. In addition to selectively screening the passage of reactants and products through pores based on size and shape, these mesoporous catalysts exert a high degree of shape-selectivity over the transition states formed within the catalyst pores. Thus, medium-pore catalysts can essentially select for the formation of specific hydrocarbon products (Froment et al., 1992).

The medium-pore zeolite ZSM-5 has been the subject of considerable study in the conversion of methanol to hydrocarbons. As synthesized, ZSM-5 has the chemical formula $Na_nAl_nSi_{96-n}O_{192}\cdot H_2O$ (Froment et al., 1992) and a pentasil unit structure (Chang et al., 1978). Oxygen linkages between these units produce 10-member ring (10-MR) channels which form the basic pore structure of ZSM-5 and other medium-pore species (Froment et al., 1992). The pore channels of ZSM-5 are depicted below in Figure 1.2.

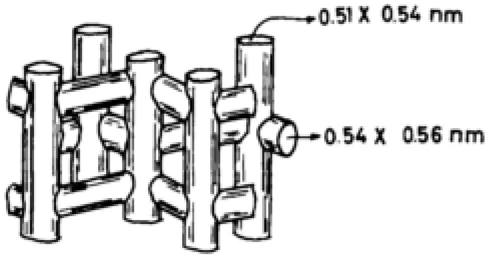

Figure 1.2 Pore Structure of ZSM-5 (Froment et al., 1992)

As can be seen from Figure 1.2, the ZSM-5 pore structure consists of intersecting zig-zag and straight channels with elliptical openings of 5.4 x 5.6 Å and 5.1 x 5.4 Å, respectively. The intersections of these channels create larger open spaces of 9 nm which are where the catalytic active sites are believed to be located. Like other zeolites, the Na cations in the ZSM-5 framework can be proton-exchanged in order to create the solid-acid form of the catalyst known as H-ZSM-5. Ion-exchanging the Al cations in ZSM-5 with other metal cations can create ZSM-5 isotypes such as Mg-ZSM-5. The conversion of methanol to hydrocarbons in ZSM-5 and other zeolites takes place primarily at Bronsted acid sites (i.e., —OH groups in the zeolite framework). Lewis acid sites are also present in the form of partially coordinated Al atoms; however, Lewis acidity is not believed to contribute significantly to MTH conversions by itself (Froment et al., 1992).

Because of its unique pore size and structure, ZSM-5 is highly selective for compounds in the gasoline-range, allowing only a small percentage of hydrocarbons with boiling points greater than about 204°C to be obtained in the liquid product (Chang et al., 1978). Furthermore, ZSM-5 suffers significantly less from coke buildup than other molecular sieve types, including other mesopourous zeolites. This resistance to coking may also be due to ZSM-5's unique shape-selectivity (Froment et al., 1992).

1.3.1.3 Small Pore Catalysts

The microporous catalysts in this class have effective pore diameters less than 4.5 Å in size and have been investigated as MTO catalysts. Examples of microporous catalysts include ZSM-34 and SAPO-34, which is similar to naturally-occurring chabazite in structure, as shown below in Figure 1.3, and has pore openings 4.3 Å in diameter (Froment et al., 1992).

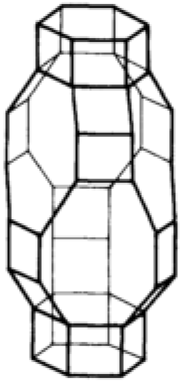

Figure 1.3 Pore Structure of Chabazite/SAPO-34 (Froment et al., 1992)

As seen in Figure 1.3, SAPO-34 pore channels consist of large (12-MR) central cages bounded by narrow (8-MR) openings which restrict nonlinear and/or C4+ hydrocarbon diffusion (Ilias & Bhan, 2013). Although similar in structure to small-pore zeolites which possess strong acidity in their protonated forms, SAPO-34 is only mildly acidic. This mild acidity, combined with a small pore size, causes SAPO-34 to be highly selective for light olefin production and more resistant to coking than microporous zeolites (Froment et al., 1992).

The central cavities of small-pore molecular sieves allow for large products such as aromatics and branched hydrocarbons to form, which are subsequently unable to escape through the narrower pore openings. Thus, deactivation occurs as the heavy coke molecules accumulate in the cages and ultimately clog the channels (Froment et al., 1992).

1.3.2 The MTH Reaction Mechanism

When the MTH reaction was first discovered, it was initially believed that hydrocarbons were formed from the concerted reaction of two or more methanol molecules, thus creating the first C—C bond. While this line of thinking has been largely abandoned in light of subsequent investigations involving hydrocarbon co-catalysts (Ilias & Bhan, 2013), the mechanism of the MTH reaction is highly complex and is still a matter of some debate, although the hydrocarbon pool mechanism has become more widely accepted (Ilias & Bhan, 2013; Olsbye, Bjørgen, Svelle, Lillerud, & Kolboe, 2005).

Currently, the hydrocarbon pool mechanism is thought to consist primarily of two interrelated cycles: an aromatics cycle and an olefins cycle (Ilias & Bhan, 2013). The overall mechanism is shown below in Figure 1.4.

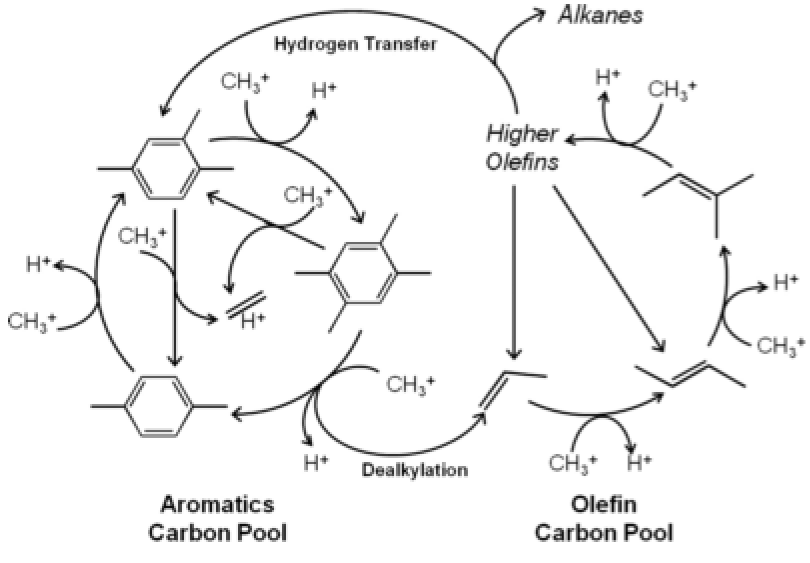

Figure 1.4 Dual-Cycle MTH Hydrocarbon Pool Mechanism (Ilias, Khare, Malek, & Bhan, 2013)

In this reaction scheme, both polymethylbenzenes and C_{3+} olefins serve as the hydrocarbon pool, or intermediate, species (Ilias & Bhan, 2013). Regardless of molecular sieve topology, polymethylbenzenes of the aromatics cycle have been identified as key hydrocarbon pool species (Olsbye et al., 2005). These polymethylbenzenes can undergo either methylation to produce more highly-substituted aromatics or dealkylation to produce ethene and other light olefins. Aromatics are methylated by the dehydration products of either methanol or DME (i.e., surface methoxide species) through a stepwise and/or co-adsorption mechanism. Dealkylation of polymethylbenzenes proceeds through a paring mechanism involving aromatic ring contraction or a side-chain methylation mechanism in which gem-methylation of polymethylbenzenes forms exocyclic double bonds which are ultimately expelled as ethene or propene. This is the primary pathway for light olefin formation in methanol conversion over SAPO-34 (Ilias & Bhan, 2013).

The olefins cycle consists of four major reaction pathways—olefin methylation, olefin cracking, hydrogen transfer and cyclization—which collectively produce light and heavy olefins, aromatics, and paraffins. Similar to the aromatic methylation pathway, olefin methylation can proceed through either a stepwise or co-adsorbed mechanism. In the stepwise mechanism, a surface methoxide adsorbed to the catalyst surface reacts with an olefin such as ethene to produce propene, whereas in the co-adsorbed mechanism methylating agent and olefin adsorb together and react with one another in a single step. Higher olefins are primarily produced via olefin methylation. Lighter olefins, on the other hand, can be produced through olefin cracking, which proceeds via alkoxide intermediate formation and β-scission (Ilias & Bhan, 2013).

Saturated hydrocarbons are formed via hydrogen abstraction and transfer from cyclic or acyclic olefins or paraffins to an adsorbed alkoxide species. The hydrogen donor may be converted into a diene or triene in the process and undergo subsequent cyclization to form an aromatic species. Cyclization can also proceed via cycloalkane formation from olefins followed by dehydrogenation to aromatics (Ilias & Bhan, 2013).

As shown in Figure 1.4, hydrogen transfer/cyclization and aromatic dealkylation unify the aromatics and olefins cycles. Although the two cycles do not proceed entirely independent of one another, zeolite structure plays a role in determining their relative influence and, therefore, the final product distribution for a given MTH reaction. In a few cases, one cycle has been shown to effectively dominate over the other. With SAPO-34, for instance, the narrow pore openings prevent the diffusion of bulky hydrocarbons from the catalyst pore cages which leads light olefins generated from aromatic dealkylation to constitute the majority of the product distribution. H-ZSM-22, on the other hand, has small one-dimensional pore channels which prevent aromatics reactions due to space limitations. Thus, olefins are the dominant hydrocarbon pool species in MTH over ZSM-22, and C_{5+} paraffins are selectively produced (Ilias & Bhan, 2013).

1.4 Effects of Operating Variables on the MTH Reaction

A number of studies have revealed the impact that changes in operating conditions can have on the final product distribution of MTH (Froment et al., 1992). The extent to which the aromatic cycle dominates over the olefin cycle, or vice-versa, can be tuned by experimental conditions. For example, Enrique Iglesia's group has demonstrated the ability to produce almost entirely branched C_4 and C_7 paraffins from zeolite H-BEA by increasing the partial pressure of DME at 473 K. By saturating the catalyst with methylating agent at low temperature, the olefins cycle is able to proceed much faster than the aromatics cycle (Ilias & Bhan, 2013).

Early studies by Mobil scientist Clarence Chang also investigated pressure effects, as well as other process variable effects, on MTH performance. Chang found that increasing the partial pressure of methanol increased the production of durene and gasoline-range hydrocarbons. Conversely, increasing temperature was found to favor the production of light olefins and paraffins and reduce the amount of durene produced (Chang et al., 1978). In a separate report, Chang and Silvestri also showed that increasing space time, or decreasing liquid hourly space velocity (LHSV), resulted in increased paraffin, aromatic and heavy olefin production. Complete methanol and dimethyl ether conversion was found to coincide with maximum C_2-C_5 olefin yield at approximately 4×10^{-2} hr (Chang & Silvestri, 1977).

1.5 Challenges of the MTH Reaction

While much progress has been made toward understanding MTH chemistry and advancing the process technology, considerable challenges remain. Among the problems associated with MTH operation are catalyst coking and heat management issues due to the exothermic nature of the reaction.

1.5.1 Catalyst Coking

As mentioned previously, all molecular sieve catalysts experience coking to various degrees in the conversion of methanol to hydrocarbons, with medium-pore catalysts such as ZSM-5 exhibiting a particularly high resistance to coke formation (Froment et al., 1992). Coke accumulated during the MTH reaction can block both catalyst active sites and pores (Bibby, Milestone, Patterson, & Aldridge, 1986), thus hindering the diffusion of both products and reactants. Considerable efforts have been undertaken by M. Guisnet and others (Benito, Gayubo, Aguayo, Olazar, & Bilbao, 1996; Bibby et al., 1986; Guisnet & Magnoux, 1989; Schulz, 2010) to understand the coking mechanism as well as the nature of the coke compounds themselves.

In one such study, Guisnet and Magnoux found that both zeolite pore structure and acidity have a significant influence on the rate of coke laydown and on the impact of coking on catalyst performance (Guisnet & Magnoux, 1989). One-dimensional zeolites and those with chabazite-like structures reportedly suffer the most from coking. Hydrofluoric acid extractions of the carbonaceous deposits from these catalysts revealed that the identities of the main coke compounds differ from one zeolite to the next, with the degree of coke aromaticity increasing with coke amount. Guisnet and Magnoux's proposed mechanism for polycyclic aromatic hydrocarbon (i.e., coke) formation is cyclization and hydrogen transfer of alkylated monoaromatics formed from olefinic cracking products.

In their commercial studies, Mobil's solution to the MTH coking problem was to maintain a series of five MTH reactors in parallel, four of which are in operation while the fifth is taken off-line for regeneration (Keil, 1999). The regeneration process, as mentioned before, consists of oxidizing the coke in air. While activity can generally be restored through coke burn-off, regeneration of the catalyst under the extreme heat of oxidation can result in degradation or even permanent activity loss (Froment et al., 1992).

1.5.2 Heat Management

Due to the exothermic nature of the MTH reaction, heat management is another major concern affecting the development of the MTH technology (Chang et al., 1978). Overall, the reaction has an adiabatic temperature rise of about 600°C (Keil, 1999). Poor temperature control due to the release of excessive reaction heat can have a negative impact on the quality of the MTH product as well as the economics of the process (Chang et al., 1978).

Mobil's strategy for managing reaction heat resulted in the complex reactor staging of the New Zealand plant and the use of a cooled light gas recycle stream to lower the effluent temperature from the methanol dehydration reactor and thus reduce the temperature rise in the MTG reactor (Keil, 1999).

Another option which can improve both heat and mass transfer in the MTH reaction is the use of a supercritical fluid reaction medium.

Chapter 2 Supercritical Fluids (SCFs) in Heterogeneous Catalysis

2.1 Advantages of SCF Reaction Media

A supercritical fluid is one whose temperature and pressure exceed the critical temperature and pressure of the substance. Supercritical fluids have physical properties which are intermediate between those of liquids and gases. For instance, SCFs have more vapor-like diffusivities and more liquid-like solubilities and heat transport properties. Another interesting feature of SCFs is that their physical properties can be tuned with changes in temperature or pressure (Huang, Elbashir, & Roberts, 2004). Figure 2.1 illustrates the pressure-dependence of SC hexane and pentane density.

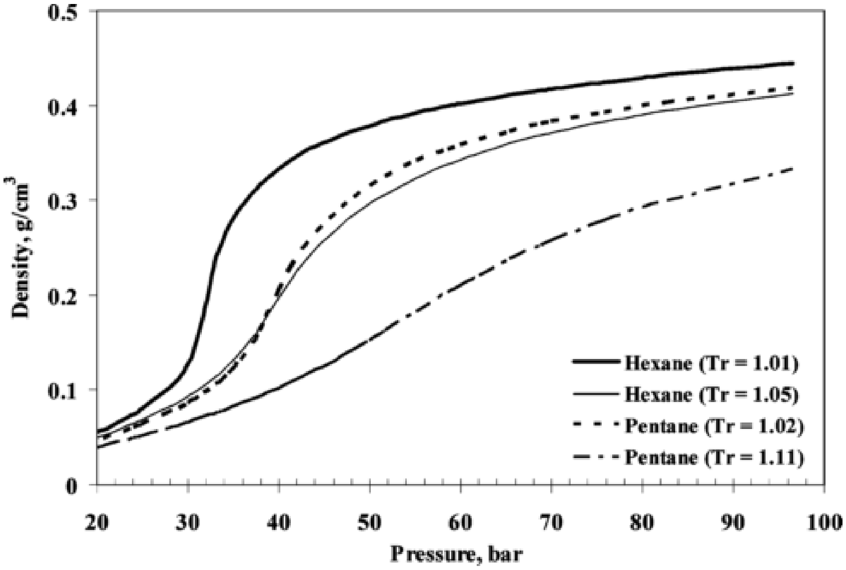

Figure 2.1 Dependence of SC Hexane and Pentane Density on Pressure (Huang et al., 2004)

The higher thermal conductivities and densities of supercritical phase substances can lend SCFs improved heat transfer and solvent strength relative to gas phase substances. Thus, SCFs can remove excess reaction heat and extract heavy products more effectively than their gas phase counterparts (Nimir O Elbashir, Bukur, Durham, & Roberts, 2010). Furthermore, the gas-like diffusivities and viscosities of SCFs reduce mass transfer limitations between gaseous reactants and liquid products, which facilitates product extraction from and reactant access to catalytic active sites in heterogeneous reactions.

SCFs have been successfully employed in a variety of exothermic, mass-transfer limited reactions such as Fischer-Tropsch Synthesis.

2.2 SCF Use in Fischer-Tropsch and Higher Alcohol Synthesis

In 1989 Yokota and Fujimoto published the first study using a supercritical hexane reaction medium to improve the reaction performance of FTS (Yokota & Fujimoto, 1989). Using hexane as an SCF reaction medium in fixed-bed FTS has been shown to reduce methane selectivity and CO_2 side product selectivity, increase yields of diesel and wax-length hydrocarbons, promote temperature uniformity in the catalyst bed, and extend catalyst lifetime compared to traditional, gas-phase FTS (Abbaslou, Mohammadzadeh, & Dalai, 2009; Nimir O Elbashir et al., 2010). Our research group has also observed the ability of SCFs to help extract and stabilize reaction intermediates such as heavy aldehydes, which are not detectable in significant quantities in gas-phase FTS (E. Durham, Zhang, & Roberts, 2010; J. E. Durham et al., 2014).

Higher alcohol synthesis from syngas, another highly exothermic polymerization reaction, has also benefited from the application of a supercritical fluid reaction medium (Jiang, Niu, & Zhong, 2001; Xu et al., 2013). In gas-phase HAS, the formation of methanol proceeds with high selectivity, while the yield and selectivity of higher alcohols such as isobutanol are poor (Herman, 2000). While methanol has a high octane value, it has low energy content relative to gasoline, and its hygroscopic nature can lead to complications in the existing transportation infrastructure such as corrosion and phase separation in the tank (Spath & Dayton, 2003). As in FTS, the use of hexane as a supercritical fluid reaction medium in HAS has been shown to decrease methane and CO_2 selectivity as well as methanol selectivity while improving the selectivity towards higher alcohols (Xu et al., 2013).

2.3 SCF Reaction Media in Zeolite-Catalyzed Reactions

While both FTS and HAS are carried out over transition metal catalysts, ethylbenzene disproportionation and ethylene oligomerization are two examples of zeolite-catalyzed reactions in which SCF media have been employed to improve performance relative to traditional, gas-phase operation. To the author's best knowledge, SCF reaction media have not thus far been employed in the conversion of methanol to hydrocarbons.

In 1998 Fujimoto's group employed n-pentane as a SC reaction medium in the oligomerization of ethylene over H-ZSM-5 (Fan, Nakamura, Ishida, & Fujimoto, 1998). The presence of SC pentane was correlated with longer catalyst lifetime and increased extraction of heavy products. Liquid pentane did not provide the same benefits as SC pentane. It was proposed that SC pentane was able to extract "catalyst poison" (i.e., C_{10+} species) from the catalyst pores, thereby forestalling deactivation. In the absence of reactant, SC pentane was also shown to have regenerative effects (i.e., 90% activity restoration) on the spent catalyst (Fan et al., 1998).

Niu and Hofmann investigated the use of supercritical fluids in the disproportionation of ethylbenzene over several types of zeolite catalysts. They found the presence of the supercritical fluid (butane or pentane) to be especially beneficial for coke extraction at low temperature conversions of ethylbenzene over zeolite Y. At high temperatures, the rate of coke laydown appears to exceed the rate of SCF extraction. For ZSM-5, which suffers from less coking issues than zeolite-Y, the coke extraction benefits of the SCF were not as pronounced; however, supercritical conditions still improved the selectivity toward diethylbenzene (DEB) over ZSM-5 while suppressing the side reaction of DEB conversion to benzene and light paraffins (Niu & Hofmann, 1996).

2.4 SCF Application Potential in MTH

Due to its exothermic nature and mass transfer limitations, MTH, like FTS, HAS, and other zeolite-catalyzed pathways, appears to be a good candidate for SCF application.

2.4.1 Potential Benefits of SCF Use in MTH

Since catalyst coking is a problem in MTH processes, the use of a SC solvent has the potential to solubilize and extract coke and coke precursors, thereby extending catalyst life—as observed in previously described investigations with zeolite reactions in SCF media. This liquid-like extraction capability coupled with gas-like SCF diffusivity can also reduce transport barriers between phases, facilitating gaseous reactant and liquid product diffusion to and from the catalyst surface.

Additionally, the improved heat transfer capabilities of a SCF environment compared to a gaseous environment should allow for efficient removal of the MTH reaction heat, which could help to simplify large-scale reactor design, reduce the risk of thermal runaway, and avoid other undesirable effects due to local overheating or poor temperature control.

2.4.2 Supercritical Solvent Selection for MTH

Selection of the appropriate SC solvent is the first important step in carrying out SCF-assisted MTH. Kaoru Fujimoto outlined several criteria for SC solvent selection in heterogeneous catalysis (Fan & Fujimoto, 1999):

1. The critical point of the solvent must be lower than the typical temperature and pressure of the reaction.
2. The solvent must be inert under the conditions of the reaction and must not poison the catalyst.
3. The solvent must be miscible with the reaction products.

Temperature is the main operating variable influencing solvent selection in SC-MTH. Since 300°C-400°C is about the typical range for MTH (Froment et al., 1992), substances with critical temperatures around 300°C are ideal candidates for SC solvents. MTH has been carried out over a wide range of operating pressures, ranging from ambient pressure to 50 atm (Chang, Lang, & Smith, 1979). Industrially, commercial and demonstration-scale MTG processes have operated at around 20 bar, as described previously. Ideally, the SC solvent would have as low a critical pressure as possible so as to minimize capital and operating costs.

Satisfying the second criterion in the above list is probably the greatest challenge in the solvent selection process. Zeolite catalysts, and H-ZSM-5 in particular, are highly active catalysts which are capable of cracking and oligomerizing even aliphatic hydrocarbons.

Only small (Giannetto, Monque, & Galiasso, 1994) or highly branched hydrocarbon species (Akolekar, 1993) can be said to be relatively unreactive over H-ZSM-5 at typical MTH temperatures. While a reactive SC solvent could still be useful for catalyst maintenance (i.e., heat removal and coke extraction), the hydrocarbon products formed from the conversion of the SC solvent will be indistinguishable from that of the methanol.

The main products of the MTH reaction are dimethyl ether (technically, a side product), hydrocarbons, and water. An ideal solvent for SC-MTH would be miscible with all of these species under reaction conditions. Fortunately, at the high reaction temperature of MTH (usually at least 300°C), the dielectric constants of the most polar compounds are greatly reduced compared to room temperature values: from about 80 to 20 for liquid water (Beaton, 1986), for example. Considering that these compounds exist as vapors at low to moderate pressure, the dielectric constants of dimethyl ether and water under MTG conditions should be even lower (e.g., about 1.4 for saturated steam at 300°C (Beaton, 1986)). Such low dielectric constant values are on par with those of nonpolar liquids, such as hexane which has a dielectric constant of about 1.88 at ambient conditions (Mopsik, 1967). Thus, a nonpolar SC solvent could theoretically be miscible with all components of the reaction mixture.

With these three criteria in mind, hydrocarbons with appropriate critical points and very low conversion levels appear to be good solvent candidates for SC-MTH. For example, isooctane (2,2,4-trimethylpentane) is a highly branched isomer of octane with a critical point of 271°C and 26 bar. Isooctane's high critical temperature is just below the lower end of MTH conditions, which means that at 300°C the density of the solvent should be sensitive to pressure changes. Because of its extensive branching, isooctane is essentially unreactive over H-ZSM-5 (Akolekar, 1993). The bulky structure of isooctane may either restrict its diffusion into the catalyst pores entirely (Choudhary & Choudhary, 1997) or allow entry but hinder isooctane's adsorption due to steric hindrance (Denayer, Souverijns, Jacobs, Martens, & Baron, 1998). If the former theory for isooctane's inertness is the case, then that would mean that isooctane would have very limited ability to extract heavy products or coke precursors from catalyst pores; however, it would still be able to dissipate excess reaction heat.

Another possible choice for SC solvent in MTH over H-ZSM-5 is butane. The critical temperature of n-butane (T_c = 152°C) is considerably lower than the MTH reaction temperature range, and the critical pressure, 38 bar, is much higher than that of isooctane. Thus, even at very high pressures, SC n-butane at 300°C will be more gas-like than liquid-like, with lower density and solvent strength as a result. Nevertheless, Yoneyama et al. observed product extraction benefits from employing SC n-butane as a SCF reaction medium over a hybrid catalyst of $CoSiO_2$/H-ZSM-5 in a combined FTS/upgrading reaction. Furthermore, they reported that at their reaction temperature of 260°C, n-butane was inert (Yoneyama, San, Iwai, & Tsubaki, 2008). While the MTH reaction temperature is about 40-100 Celsius degrees higher, even at 500°C the conversion of n-butane over H-ZSM-5 is only about 45%. The conversion of isobutane is even lower, at only 23.6% (Ono, 1992), probably due to the lower reactivity of branched compounds over H-ZSM-5. An additional benefit of using butane, which is a vapor at ambient conditions, is ease of SC solvent removal and recycle.

Ultimately, solvent selection depends on the MTH catalyst in question. Although conversion of isooctane is only 0.3% over H-ZSM-5, over large-pore catalyst MAPO-36, isooctane conversion is much higher at 33.8% (Akolekar, 1993). In general, though, for the same degree of substitution, longer chain hydrocarbons have lower diffusivity (Choudhary, Nayak, & Mamman, 1992) but higher adsorption enthalpy (Denayer et al., 1998) than shorter chain species.

Chapter 3 Investigation of Supercritical Isooctane as a Reaction Medium in the Conversion of Methanol to Hydrocarbons over H-ZSM-5

Abstract

High yields of high-octane gasoline have been achieved by carrying out the methanol-to-hydrocarbons (MTH) reaction over zeolite catalyst H-ZSM-5. However, catalyst deactivation due to coking as well as heat management challenges due to the exothermic nature of the reaction hinder utilization of MTH technology. Supercritical fluid (SCF) reaction media have been employed in heterogeneous catalysis in order to facilitate heat removal and heavy product extraction from catalyst active sites. This particular study explores the feasibility of using SCF media to enhance MTH reaction performance relative to traditional, gas-phase operation. Conversion of methanol over H-ZSM-5 was carried out in a continuous fixed-bed reactor in the presence of supercritical isooctane. Isooctane was selected as the SCF medium primarily because of its low reactivity over H-ZSM-5. The performance of SCF-assisted MTH was compared with that of gas-phase MTH at both 300°C and 370°C. Relative to gas phase operation at the same conditions, the use of supercritical isooctane resulted in improved catalyst maintenance and increased hydrocarbon productivity with increasing time on stream.

Keywords: Methanol-to-Hydrocarbons, Supercritical Fluid, H-ZSM-5, Isooctane

3.1 Introduction

Considerable research efforts have been devoted to the production of fuels and high-value chemicals from petroleum alternatives. In the X-to-Liquids, or XTL, process alternative carbon resources such as natural gas are thermochemically converted to liquid transportation fuels and other chemicals. The XTL process begins with either gasification or reforming of the carbon resource to produce a mixture of carbon monoxide and hydrogen collectively referred to as synthesis gas, or syngas. This syngas can then undergo a variety of thermochemical conversion pathways to produce the desired end product. One such pathway is methanol synthesis.

Methanol synthesis from syngas proceeds with high selectivity and is a mature commercial technology (Spath & Dayton, 2003). Current global demand for methanol is approximately 65 million metric tons per year (MI, 2014). While methanol is an important basic chemical, its corrosiveness, hygroscopic nature, and low solubility in gasoline make it unattractive for use as a standalone fuel or fuel additive with our existing transportation infrastructure (Spath & Dayton, 2003).

A few decades ago, research scientists at Mobil (now ExxonMobil) discovered that methanol can be dehydrated over zeolite catalysts to produce aliphatic and aromatic hydrocarbons with boiling points in the gasoline range (Chang, Silvestri, & Smith, 1975). The catalyst of choice for the methanol-to-gasoline (MTG) conversion is Mobil catalyst ZSM-5, which can produce high yields (>75 wt%) of high-octane gasoline from methanol (Chang et al., 1978). This high selectivity toward gasoline-range species is the result of ZSM-5's unique pore structure, which exerts both size and shape selective control over reaction products and intermediates. Manipulation of operating variables such as temperature can shift the product distribution over ZSM-5 more toward dimethyl ether (DME) or light olefins (Chang et al., 1978; Froment et al., 1992; Stocker, 1999). The MTO (methanol-to-olefins) and MTG processes are collectively referred to as methanol-to-hydrocarbons (MTH).

Although the MTH reaction is capable of selectively producing high quality gasoline, catalyst coking and heat management issues, among others (Stocker, 1999), present challenges in implementing this technology. One of the major challenges of the MTH reaction is coking (Olsbye et al., 2005). High reaction temperatures lead to rapid coke accumulation and subsequent catalyst deactivation with increasing time on stream (Benito et al., 1996). Past solutions to remove coke have involved taking reactor units offline and burning off coke in air (Keil, 1999); however, repeated cycles of coke burnoff can reduce catalyst activity over time (Gayubo et al., 1997). In addition, the highly exothermic nature of the reaction presents challenges with regards to heat removal and thermal uniformity (Chang et al., 1978). In Mobil's commercial MTG process (later abandoned), a light gas recycle and a two-reactor design strategy for the step-wise release of reaction heat were implemented for the purpose of controlling temperature rise (Keil, 1999).

Supercritical fluid (SCF) reaction media have been employed in other exothermic, mass-transfer-limited reactions such as Fischer-Tropsch Synthesis (FTS) (Nimir O Elbashir et al., 2010) and Higher Alcohol Synthesis (HAS) (Xu et al., 2013) to facilitate heat removal and heavy product extraction. Because the physical properties of SCFs are intermediate between those of a liquid and a gas, supercritical phase operation allows for a single phase environment in which liquid reaction products are readily extracted due to the liquid-like solvating ability of the SCF and through which gaseous reactants can readily diffuse due to the vapor-like diffusivity and viscosity of the SCF medium (Baiker, 1999). In addition to the benefits observed from SCF use in FTS and HAS, SCF reaction media have been shown to have an ameliorating effect on reaction performance and catalyst coking in other reactions catalyzed by ZSM-5, such as ethylene oligomerization (Fan et al., 1998) and ethylbenzene disproportionation (Niu & Hofmann, 1996).

To the author's best knowledge, SCF media have not been previously employed in the MTH reaction. Several useful criteria have been proposed (Fan & Fujimoto, 1999) to guide SCF selection in FTS:

(1) The critical point of the SCF should be below the reaction temperature and pressure.

(2) The SCF should be inert under the reaction conditions.

(3) The SCF should be miscible with the reaction products.

Based on the above criteria, hydrocarbon solvents with a critical temperature around 300°C and a low critical pressure are good potential candidates for application in MTH. The strong acidity of MTH catalysts, especially ZSM-5, presents a considerable challenge to SC solvent selection because even paraffinic hydrocarbons are reactive over these catalyst systems (Anderson, Foger, Mole, Rajadhyaksha, & Sanders, 1979). Previous studies from the literature have indicated that isooctane (critical point: 271°C, 26 bar) has very low reactivity over ZSM-5, as a consequence of its bulky structure (Akolekar, 1993). The highly-branched structure of isooctane could hinder its diffusion into the microporous channels of ZSM-5 (Choudhary & Choudhary, 1997); however, despite isooctane's mass transfer limitations, its low reactivity coupled with its relatively high critical temperature make it a good candidate for this pioneering study involving SCF application in the MTH reaction.

3.2 Experimental

3.2.1 Catalyst Preparation

The commercial ZSM-5 (ammonium) powder used in this study was purchased from Alfa Aesar (Product No. 45879, CAS #1318-02-1) and has a reported Si/Al ratio of 23:1 and surface area of 425 m^2/g. The ammonium ZSM-5 catalyst was converted to H-ZSM-5 through calcination in air at 550°C for 12 hours. The H-ZSM-5 powder was then compressed into pellets using 5000 lb_f and sieved to obtain catalyst particles that were 45-70 mesh (210-354 microns) in size.

N_2 sorption studies of the H-ZSM-5 particles before and after reaction were conducted at -196°C using a Micromeritics TriStar II 3020 surface area analyzer. Prior to conducting N_2 sorption studies, catalyst samples were degassed for 5 h at 150°C in helium using a Micromeritics SmartPrep degas system.

Powder X-Ray diffraction (XRD) spectra of the catalyst samples were obtained using a Bruker D8 advanced diffractometer with a Cu K_α source. Catalyst samples were scanned over the 2θ range 5° to 90° at a scan speed of 0.1 s/step.

Thermogravimetric analysis (TGA) was carried out to determine the coke content of the post-reaction catalyst samples. Approximately 25-45 mg of used catalyst was loaded in a platinum TGA pan and analyzed using a TA Instruments Q5000 sorption analyzer. Temperature was ramped at a rate of 10°C/min to 120°C and held constant for 20 min to allow for desorption of water. Temperature was then ramped at 10°C/min to 600°C and held constant for 3 hours to ensure complete burn-off of accumulated coke.

3.2.2 Catalyst Testing

A schematic of the reactor system used in this series of studies is shown below in Figure 3.1. In this reactor setup, methanol (BDH, ACS grade) is introduced into the system via a HPLC pump (Chrom Tech, Series III) at 0.1 mL/min and preheated prior to entering the fixed bed reactor, which contains 1g of H-ZSM-5 packed between layers of glass wool. Reaction pressure is controlled via a Straval back pressure regulator (Model BPH0502T-N2403). In addition to the reactant methanol, 10 SCCM of N_2 (Airgas, ultra high purity grade) is passed through the reactive zone by means of a mass flow controller (Porter

Instrument, Series II). This N_2 flow serves as an internal standard in vapor product analysis.

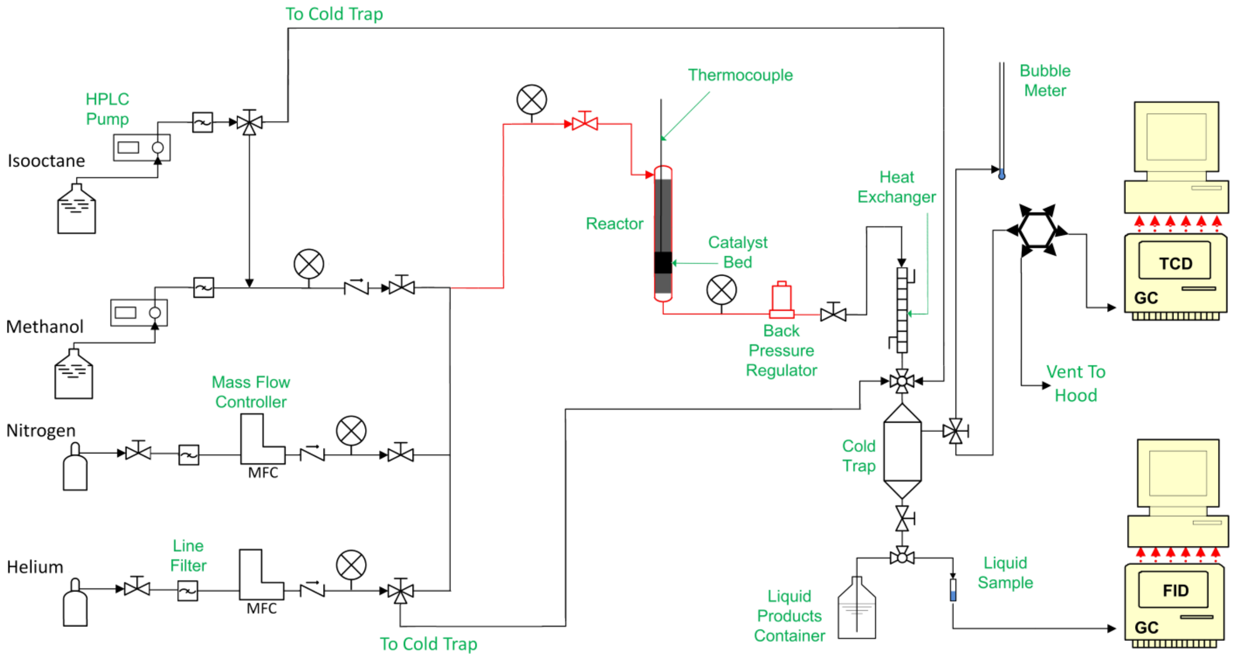

Figure 3.1 Schematic of supercritical MTH reactor system

For gas phase MTH studies, isooctane (J.T.Baker, HPLC grade, 99.8% purity) is introduced through a reactor bypass line at 0.5 mL/min using an HPLC pump (LabAlliance brand). The isooctane collects in the cold trap and serves as a liquid "trap" for the MTH products and as a solvent for subsequent GC analysis. For supercritical phase MTH studies, isooctane is passed through the reactive zone at a flow rate of 1.22 mL/min (3:1 molar ratio of SC isooctane to methanol).

For both gas phase and supercritical phase studies, 50 SCCM of He (Airgas, ultra high purity grade) is metered directly to the cold trap via a mass flow controller (Brooks 5850E) for the purpose of diluting the effluent vapor stream prior to GC analysis. This allows for the accurate quantification of the N_2 internal standard concentration as well as the concentrations of vapor products.

The reactor consists of a 316 stainless steel tube (HIP 20-LM9-8, ID 0.8 cm, length 20.5 cm), the top 13 cm of which serves as a preheating zone. The entire reactor is maintained at reaction temperature (either 300°C or 370°C in this work) by means of 1/16" stainless steel thermocouple (Omega, KTSS-116G-12) and Omega temperature controllers (Model CSC32). Heat is supplied to the reactor via heating tape (Omegalux, FGH051-020). The reaction pressure, as well as the pressure in other areas of the apparatus, is measured via Dwyer pressure gauges (Model DPG-110).

A heat exchanger and cold trap are used to collect and separate the liquid products from the vapor products, which are analyzed separately using gas chromatography. The cold trap is maintained at 0°C and ambient pressure. Vapor products are injected via a 10-port automatic injection valve (Valco Instrument) with a 2-mL sample loop and are analyzed online using a SRI 8610C gas chromatograph (GC) equipped with a 30-ft Hayesep DB packed column (Agilent) and thermal conductivity detector (TCD). Liquid products are collected from the cold trap periodically and analyzed using a GC (Bruker 430-GC) with a 30-ft DB-5 capillary column and flame ionization detection (FID).

3.2.3 Product Analysis

Permanent gases N_2, CO, and CO_2 as well as C1-C4 hydrocarbons are analyzed online using a GC-TCD with a Hayesep DB packed column and PeakSimple software. Liquid products are collected from the cold trap in two phases: an aqueous "bottom phase" consisting primarily of water, methanol (MeOH), and dimethyl ether (DME) and an organic "top phase" consisting primarily of isooctane, which contains the majority of the liquid hydrocarbon species. A GC-FID equipped with a DB-5 capillary column and CompassCDS software is used to analyze both top and bottom phase products, which range from 3 to 12 carbons in number.

Vapor product concentrations are quantified using gas response factors (RFs). The response factor of a given vapor product (RF_i) is calculated as follows:

$$RF_i = \frac{C_i}{A_i}$$

where C_i is the molar concentration of species i and A_i is the corresponding TCD area. With the exception of N_2, molar concentrations of a given vapor product are determined from Airgas certified calibration standards. The molar concentrations of analytes in these standards are similar to those observed in MTH.

Since N_2 is the internal standard, for maximum accuracy its RF is recalculated prior to the start of each reaction based on the known concentration of N_2 in He diluent. This known concentration of N_2 is determined from the MFC-regulated flowrates of N_2 and He, which are verified using a bubble flowmeter. Each gas RF is the average of at least three RFs obtained from separate injections.

With N_2 as an internal standard of fixed molar flowrate m_{N_2}, the molar flowrates (m_i) for each individual vapor product in the reactor effluent can be determined as follows:

$$m_i = A_i \times RF_i \times \frac{m_{N_2}}{C_{N_2}}$$

where C_{N_2} is the molar concentration of N_2 in the effluent vapor.

Liquid product mass concentrations are quantified using a combination of area normalization method (Dietz, 1967) and calibration curves. For top phase samples, area normalization is used exclusively. This calculation method assumes that the water concentration in the top phase organic samples is negligible and is described as follows:

$$c_i = \frac{A_{a,i}}{\sum A_{a,i}}$$

where c_i is mass concentration and $A_{a,i}$ is the adjusted peak area.

Areas are adjusted by dividing the FID peak area by a relative response factor (RRF), which for most hydrocarbons is approximately 1 (Dietz, 1967). The RRFs employed for methanol and DME are 0.23 (Dietz, 1967) and 0.418, respectively. The DME RRF was obtained by dividing the methanol RRF by a correction factor of 0.55, which was previously determined experimentally by Chen et al. (J. Chen, Zhang, Yang, & Cai, 1997).

Methanol mass concentration in the aqueous bottom phase is determined using the following methanol-in-water calibration curve, shown in Figure 3.2.

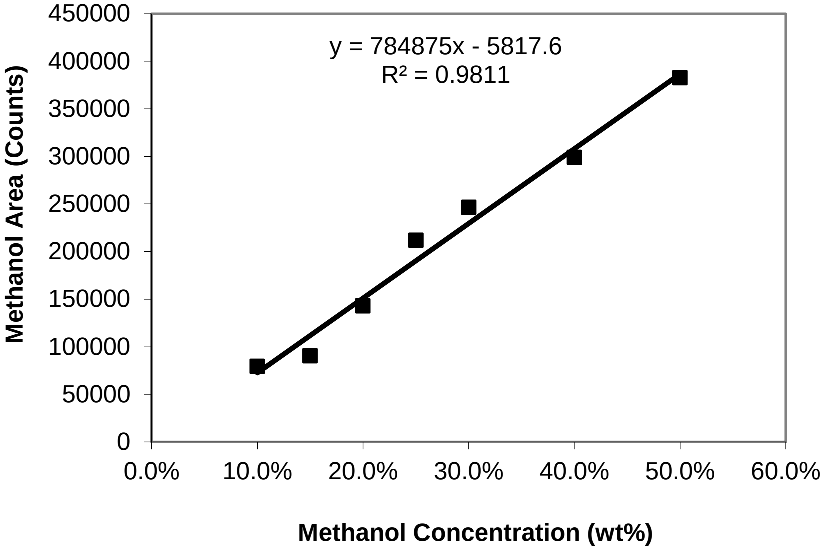

Figure 3.2 Calibration curve for methanol in water for Bruker 430 GC-FID

The mass concentrations of DME and trace hydrocarbons in the bottom phase samples are then determined by scaling the known methanol concentration with the appropriate peak area and RRF. Taking DME as an example, the bottom phase concentration of DME ($c_{DME,b}$) is calculated as follows:

$$c_{DME,b} = c_{MeOH,b} \times \frac{RRF_{MeOH}}{RRF_{DME}} \times \frac{A_{DME}}{A_{MeOH}}$$

Since the vast majority of hydrocarbon products partition into the top organic phase, the concentrations of hydrocarbon species in the bottom aqueous phase are considered negligible in this work.

3.2.4 Experimental Procedures

After loading the fixed-bed reactor with 1g of 45-70 mesh H-ZSM-5 catalyst, the system was pressure-tested overnight at 100 psig above the reaction pressure to ensure that no leaks were present in the system. The calibration of the N_2 and He MFCs was also checked using a bubble flowmeter.

Prior to reaction, the system was heated and pressurized overnight to reaction conditions using approximately 40 SCCM of N_2. The hot N_2 flow also served to pre-condition the catalyst for reaction. After achieving reaction pressure, the N_2 flowrate was reduced to the reaction setpoint of 10 SCCM.

In gas phase studies, reaction was initiated by introducing methanol at 0.1mL/min (WHSV 4.75 h^{-1}) to the preheating zone. Isooctane bypassed the reactive zone and was metered to the cold trap at 0.5mL/min. In the supercritical isooctane studies, isooctane was first passed over the catalyst bed at 1.22 mL/min (3:1 molar ratio of isooctane to methanol) for 30 min to 1 h prior to methanol introduction.

The 316 stainless steel tubing preceding the reactor was heated to a temperature of 145°C in order to vaporize the liquid methanol feed. Because the small diameter tubing in this liquid preheat region catalyzes the thermal decomposition of methanol, higher temperatures in this zone could not be employed. In SC MTH, this tubing served as a premixing area for the isooctane, methanol, and N_2 feed.

The temperature in the reactor was maintained at either 300°C or 370°C, depending on the temperature setpoint for a particular study. With the catalyst bed positioned 3 cm from the bottom of the reactor, the top portion of the reactor allowed the feed gas to be preheated to reaction temperature prior to contact with the catalyst. It is important to note that the reactor, due to its larger diameter, was not catalytically active for methanol decomposition at either 300°C or 370°C, as verified by blank reactor runs conducted over this temperature range.

For gas phase and supercritical isooctane phase studies, system pressure was set at 235 psig and 835 psig, respectively. These pressure setpoints were selected in order to maintain methanol partial pressure at approximately 200 psig.

In all four MTH studies, the total reaction time on stream was approximately 50 h. Vapor and liquid samples were taken at 2-hour intervals for the first 8 hours and then at intervals of up to 12 hours for the remainder of the experimental run. Vapor samples were taken by online injection and represent the gas product composition at a single time point in the reaction; however, since liquid products were analyzed offline, liquid was allowed to accumulate in the cold trap between samples. Thus, the liquid product concentrations obtained are essentially the average concentrations for the sample period.

Following reaction, hot N_2 was passed through the system overnight to flush out any remaining liquid and gas in the system and to dry the catalyst. After drying, the reactor was dismantled so that the catalyst could be retrieved for post-reaction catalyst characterization.

3.3 Results and Discussion

3.3.1 Effect of Temperature and Supercritical Isooctane on MTH Reaction Performance

In the following set of studies, reactant conversion and product distribution were investigated in gas phase (GP) and supercritical (SC) isooctane phase environments at two different reaction temperatures, 300°C and 370°C. Temperature has a strong effect on MTH reaction performance (Froment et al., 1992), with the product distribution varying widely over the typical MTH temperature range, 300-400°C. As such, these two reaction temperatures were selected in order to give a better understanding of supercritical isooctane's effect as a reaction medium near the "low" and "high" ends of the MTH temperature spectrum. Furthermore, the properties of SC isooctane vary with temperature. At 300°C, isooctane is in close proximity to its critical temperature (271°C) and should behave more as a dense liquid-like fluid (Baiker, 1999), while at 370°C the SC isooctane will be more vapor-like, with higher diffusivity but lower density. Thus, the relative impact of the SC isooctane reaction medium on MTH performance could vary greatly depending on reaction temperature.

3.3.1.1 Reactant Conversion

The conversion of methanol to hydrocarbons with time on stream (TOS) is shown below in Figure 3.3 and Figure 3.4, for reaction at 300°C and 370°C, respectively. In this conversion calculation, dimethyl ether (DME) is treated as unconverted reactant, as follows:

$$conv.\ (\%) = \left[1 - \frac{[methanol\ out\ (mol) + 2\ \times\ DME\ out\ (mol)]}{methanol\ in\ (mol)}\right] \times 100$$

Since liquid products were collected manually, the conversion values displayed in the following figures represent the average methanol conversion over the time interval between liquid samples.

At 300°C, methanol conversion to hydrocarbons under both gas phase and SC isooctane phase conditions remained relatively stable for the duration of the 50-h TOS studies. Average methanol conversions were approximately 51% and 55% for GP and SC MTH, respectively. The stable conversion maintained during the course of the 300°C reactions is most likely due to the low hydrocarbon and consequently low coke formation at this lower end of the MTH temperature range. Below about 315°C, the conversion of methanol and its dehydration product dimethyl ether (DME) to hydrocarbons is incomplete (Chang et al., 1978). This also accounts for the fact that methanol conversion under both GP and SC isooctane phase conditions remained well below 100%, even near the start of the reaction at 2h TOS. Dimethyl ether is the major product formed at this lower MTH temperature. Overall, conversion to hydrocarbons remained slightly elevated under supercritical isooctane conditions, which shows that the presence of the supercritical isooctane does not appear to have an adverse effect on catalytic activity at 300°C.

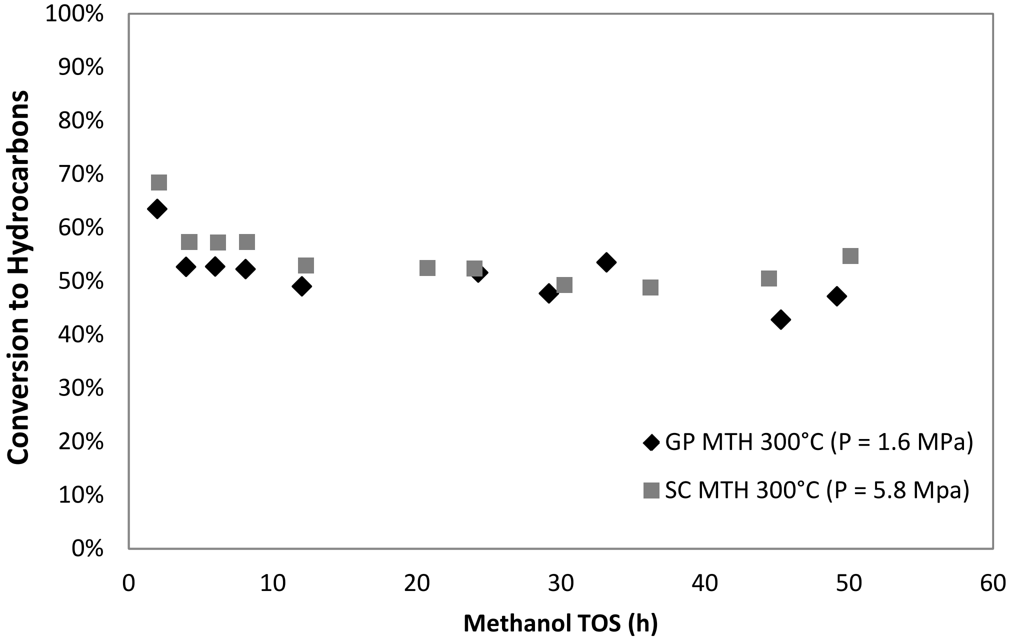

Figure 3.3 Methanol conversion to hydrocarbons over H-ZSM-5 at 300°C. Reaction conditions were as follows: catalyst = H-ZSM-5 (Si/Al = 23), $WHSV_{methanol}$ = 4.75 h^{-1}, $P_{methanol}$ = 1.4 MPa, isooctane/methanol = 3 (molar ratio; SC study only)

Figure 3.4 shows the methanol conversion to hydrocarbons for the gas phase and SC isooctane phase reactions conducted at 370°C. At this temperature, the MTH catalyst is more active, with the conversion of methanol essentially going to completion for the first 12 hours TOS under GP conditions. Between 24 and 50 hours TOS, conversion to hydrocarbons in the gas phase dropped abruptly from 96% to 44%. This decrease in GP MTH conversion coincided with an increase in the production of DME, which indicates a decline in catalyst activity beginning at around 24 hours TOS, most likely as a result of pore filling. In the presence of SC isooctane, methanol conversion to hydrocarbons showed a steady but gradual decline with TOS and appeared to stabilize around 46% by the end of the study. This suggests that the SCF medium may allow for more controllable catalytic deactivation, which could be due to better extraction of coke and/or reaction heat by the supercritical solvent. Lower conversion under supercritical conditions at 370°C could be due to increased isooctane reactivity at this higher reaction temperature, which could lead to increased active site competition for the reactant methanol, therefore resulting in an apparent decrease in catalytic activity.

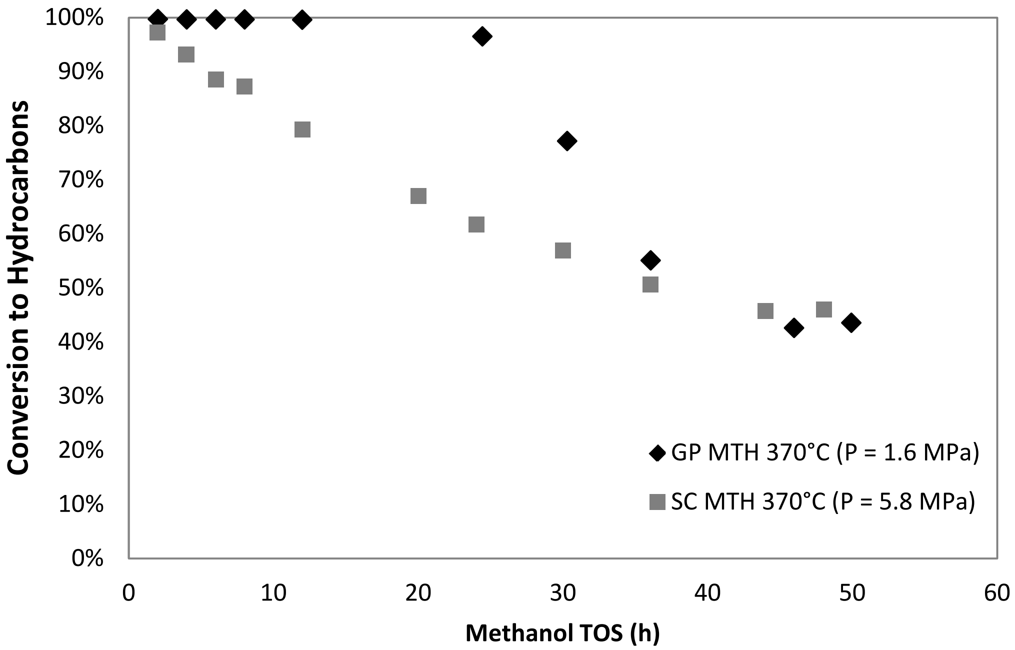

Figure 3.4 Methanol conversion to hydrocarbons over H-ZSM-5 at 370°C. Reaction conditions were as follows: catalyst = H-ZSM-5 (Si/Al = 23), $WHSV_{methanol}$ = 4.75 h^{-1}, $P_{methanol}$ = 1.4 MPa, isooctane/methanol = 3 (molar ratio; SC study only)

3.3.1.2 Product Distribution

The vapor products of the MTH reaction at 300°C are shown below in Figure 3.5 and Figure 3.6, as a function of methanol time-on-stream. Under gas phase conditions (Figure 3.5), the carbon selectivity toward hydrocarbons at 2h TOS was slightly above 1%, with light olefins constituting the majority of the hydrocarbon product distribution. Hydrocarbon selectivity in the vapor product declined steadily throughout the course of the gas phase investigation. By 50 hours TOS, the total hydrocarbon selectivity fell to around 0.2%, with the selectivity toward light olefins and paraffins becoming approximately equal at 50h TOS. The initial DME selectivity was high at around 33%. This is attributed to the incomplete conversion of methanol and DME to hydrocarbons at temperatures below 315°C (Chang et al., 1978). Between 4 and 50 hours TOS, the DME selectivity increased monotonically to about 45%. Increasing DME selectivity is indicative of catalyst deactivation (Bibby et al., 1986).

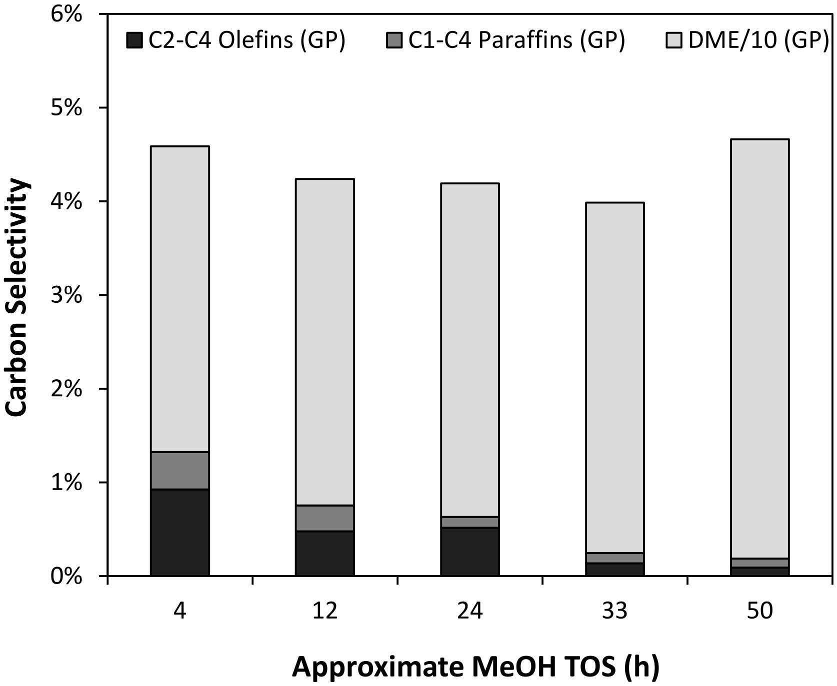

Figure 3.5 Vapor product distribution for GP MTH at 300°C. Reaction conditions were as follows: catalyst = H-ZSM-5 (Si/Al = 23), $\text{WHSV}_{\text{methanol}}$ = 4.75 h^{-1}, P_{methanol} = 1.4 MPa, isooctane/methanol = 3 (molar ratio; SC study only)

Compared to gas phase conditions at the same temperature, hydrocarbon selectivity in the presence of supercritical isooctane remained consistently higher throughout the 50h study, as shown below in Figure 3.6. While light olefin selectivity declined gradually between 4h and 50h TOS, light paraffin selectivity actually increased in the latter half of the supercritical study, from 0.35% at 12h to 1.54% at 24h. In contrast to the gas phase study, DME carbon selectivity in the vapor phase remained much lower, increasing only moderately from about 20% to 25% between 4h and 36h TOS before appearing to level off at around 25% for the last 14 hours of the study. Relative to gas phase operation at 300°C, conducting the MTH reaction in the presence of SC isooctane promotes the production of light hydrocarbons.

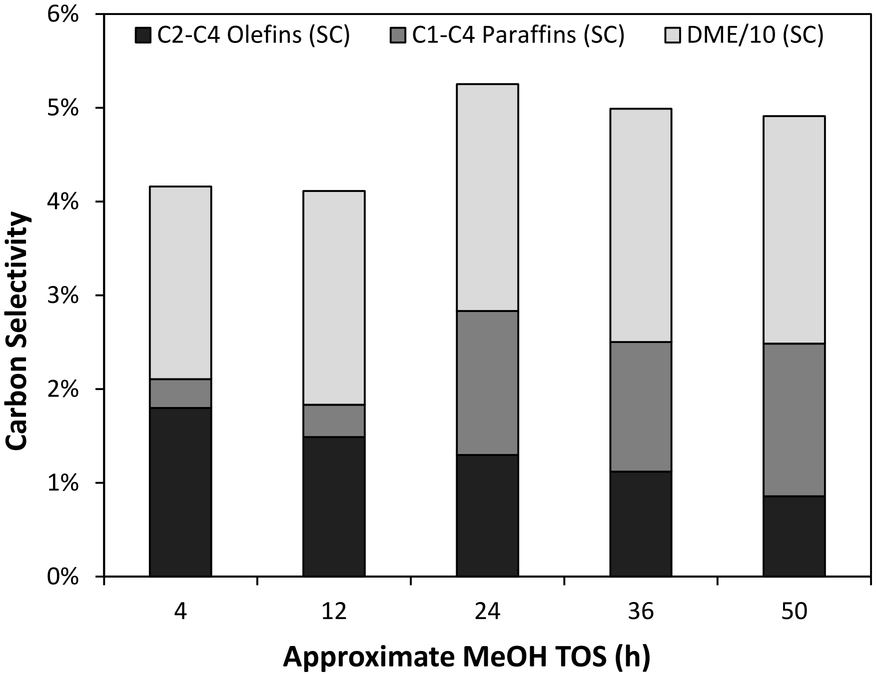

Figure 3.6 Vapor product distribution for SC MTH at 300°C. Reaction conditions were as follows: catalyst = H-ZSM-5 (Si/Al = 23), $WHSV_{methanol} = 4.75\ h^{-1}$, $P_{methanol} = 1.4$ MPa, isooctane/methanol = 3 (molar ratio; SC study only)

The vapor product distributions for MTH reactions carried out at 370°C are shown below in Figure 3.7 and Figure 3.8. For both gas phase and SC isooctane phase experiments, the carbon selectivity toward hydrocarbons was significantly higher at 370°C than at 300°C. Under gas phase conditions (Figure 3.7), light paraffin selectivity declined monotonically throughout the course of the 50-h TOS study, from 7.95% at 2h TOS to 0.29% at 50h TOS. Olefin selectivity, on the other hand, remained relatively stable at around 5% between 4h and 12h TOS, increased to 7.65% between 12h and 24h TOS, and finally decreased to 0.04% between 24h and 50h TOS. DME first appeared in the vapor product at 24h TOS. From 24 to 50h TOS, DME carbon selectivity increased from 2.19% to 36.46%, indicating a sharp decline in MTH catalyst activity, most likely as a result of increasing acid site blockage by internal coke, the laydown of which is accelerated at higher reaction temperatures (Benito et al., 1996).

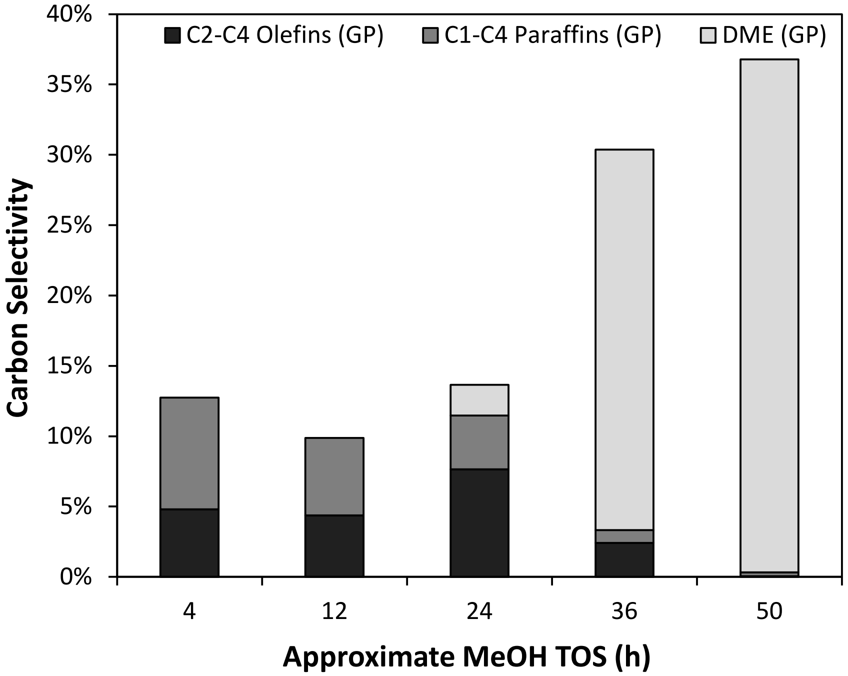

Figure 3.7 Vapor product distribution for gas phase MTH at 370°C. Reaction conditions were as follows: catalyst = H-ZSM-5 (Si/Al = 23), $\text{WHSV}_{\text{methanol}}$ = 4.75 h^{-1}, P_{methanol} = 1.4 MPa, isooctane/methanol = 3 (molar ratio; SC study only)

While initial light hydrocarbon selectivity at 370°C was lower under supercritical isooctane conditions compared to gas phase conditions, the decline in hydrocarbon selectivity with increasing TOS was much less severe. Over the course of the 50-h experiment, total hydrocarbon selectivity decreased from 9.24% to 5.58%. By 36h TOS, Figure 3.8 indicates that the carbon selectivity toward hydrocarbons in the presence of the SCF reaction medium (5.99%) was nearly twice that observed with no SC isooctane present (3.32%). The appearance of DME in the product distribution early on in the reaction may be due to the extractive or diluent effects of the SCF medium, which could remove DME from the catalyst surface before it has the opportunity to undergo further dehydration to hydrocarbons. However, although DME breakthrough occurs much earlier in SC MTH than in GP MTH, the increase in DME carbon selectivity in the vapor phase is much more gradual in SC MTH, and the final DME selectivity at 50h TOS (15.14%) is less than half that observed under GP conditions. Additionally, as in SC MTH at 300°C, at 370°C the light paraffin selectivity showed a slight increase with TOS after 12h.

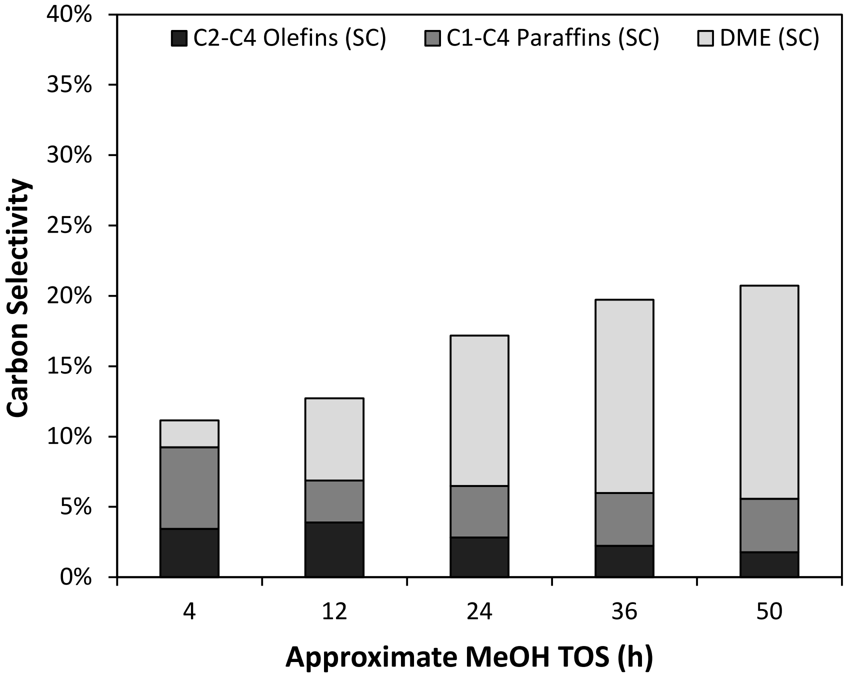

Figure 3.8 Vapor product distribution for SC isooctane MTH at 370°C. Reaction conditions were as follows: catalyst = H-ZSM-5 (Si/Al = 23), $WHSV_{methanol} = 4.75\ h^{-1}$, $P_{methanol} = 1.4$ MPa, isooctane/methanol = 3 (molar ratio; SC study only)

The liquid products of the MTH reaction consisted of two phases: a top phase consisting primarily of the solvent isooctane and a bottom aqueous phase containing methanol, DME, and trace hydrocarbons. The majority of the liquid hydrocarbon and dissolved gaseous hydrocarbon products were retained in the top phase. The total yields of hydrocarbons in the top liquid phase are shown below in Figure 3.9 and Figure 3.10, for 300°C and 370°C, respectively.

In general, liquid hydrocarbon yield at 300°C decreased steadily with TOS for both GP and SC isooctane phase operation. Between 4 and 50h TOS, liquid hydrocarbon yield declined from 0.07 to 0.007 g/h under gas phase conditions. Hydrocarbon production in SC MTH, however, remained consistently higher than in GP MTH, decreasing from 0.17 to 0.05 g/h over the course of the 50-h study. Between 36h and 50h TOS, the yield of hydrocarbons even appeared to stabilize around 0.05 g/h under SC MTH conditions, while under gas phase operation, hydrocarbon yield over this time interval continued to decline from 0.01 to 0.007 g/h. Clearly, the production of liquid hydrocarbons is enhanced by operating the MTH reaction in a supercritical isooctane environment. While hydrocarbon production could be inflated by the reactivity of the SC isooctane medium, most likely the improved liquid hydrocarbon yield observed under SC MTH conditions is the result of improved catalyst maintenance due to extraction of coke or coke precursors by the SCF.

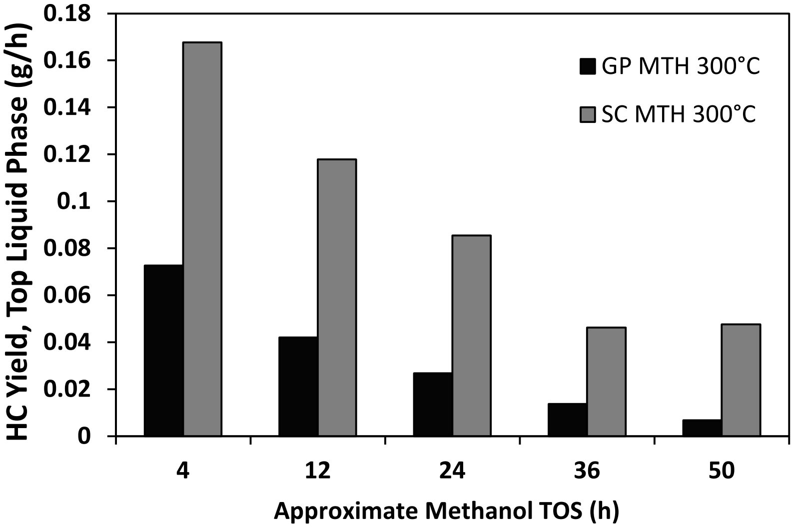

Figure 3.9 Yield of hydrocarbon products in the top liquid phase at 300°C (*GP yield actually for 33h TOS). Reaction conditions were as follows: catalyst = H-ZSM-5 (Si/Al = 23), WHSV$_{methanol}$ = 4.75 h^{-1}, P$_{methanol}$ = 1.4 MPa, isooctane/methanol = 3 (molar ratio; SC study only)

Figure 3.10 shows hydrocarbon yield with TOS for reaction at 370°C. Overall, hydrocarbon production was greatly enhanced at 370°C compared to 300°C, owing to the fact that reactant conversion in MTH can go to completion at this higher reaction temperature (Chang et al., 1978). The trends in liquid hydrocarbon yield with TOS closely mirror those shown in Figure 3.4 for methanol conversion. While at 4h TOS hydrocarbon yields in both GP and SC MTH were approximately 1.37 g/h, GP yield surpassed that of SC MTH at 12h and 24h TOS before an apparent decline in catalytic activity led to a sharp decrease in GP MTH yield between 24h and 36h TOS. From 36h onward, hydrocarbon production in the presence of SC isooctane surpassed that of GP MTH, suggesting that the SCF medium promotes more stable reaction performance with increasing TOS. The decline in catalytic activity under SC MTH conditions, though monotonic, was gradual and less severe compared to that observed in GP MTH. By 50h TOS, liquid hydrocarbon production in GP MTH dropped over 97% from a peak value of 1.48 g/h, while under SC MTH conditions, hydrocarbon yield fell 85% over the course of 50h TOS.

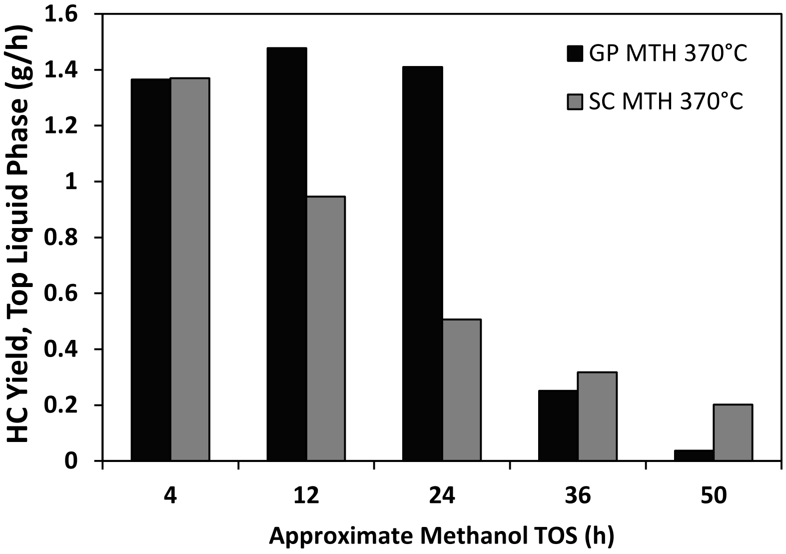

Figure 3.10 Yield of hydrocarbon products in the top liquid phase at 370°C. Reaction conditions were as follows: catalyst = H-ZSM-5 (Si/Al = 23), $\mathrm{WHSV}_{\mathrm{methanol}}$ = 4.75 h^{-1}, P_{methanol} = 1.4 MPa, isooctane/methanol = 3 (molar ratio; SC study only)

Figure 3.11 shows the gas phase liquid product distribution as a function of both carbon number and TOS. At 300°C, dissolved light hydrocarbons (C3-C6) constituted 58% of the initial (4h TOS) liquid product distribution in the gas phase; however, with increasing time on stream, the product spectrum shifted toward heavy product formation, as evidenced by the predominance of C9+ hydrocarbons at 50h TOS. By the end of the 300°C study, 61% of the GP liquid product distribution consisted of C9+ hydrocarbon species, the majority of which were methylated aromatics such as durene (1,2,4,5-tetramethylbenzene). A similar trend was observed in the liquid product distributions at 370°C. Under gas phase conditions, the initial products at 370°C were more evenly distributed between light, intermediate, and heavy hydrocarbons than at 300°C. However, as at 300°C, by 50h TOS the percentage of light hydrocarbons in the liquid product decreased while the relative amounts of C6-C9 and C9+ products increased to 55% and 42%, respectively. This observation of increasing C6+ product with MTH catalyst aging has been previously reported in the literature (Chang et al., 1978; Keil, 1999).

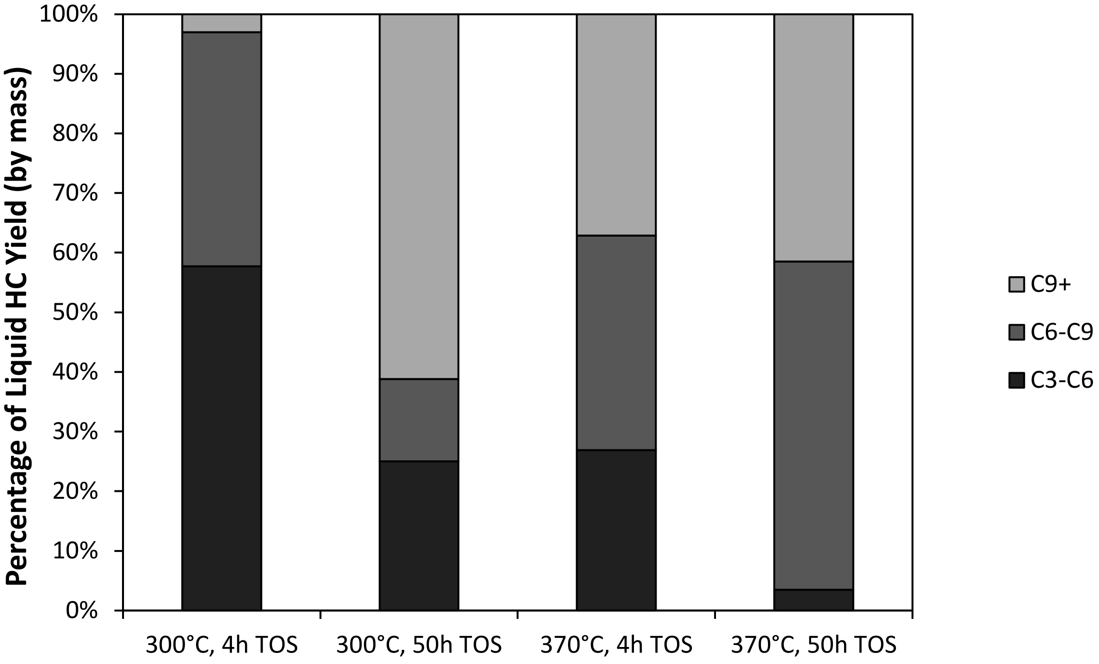

Figure 3.11 Gas phase hydrocarbon product distribution by carbon number in the top liquid phase. Reaction conditions were as follows: catalyst = H-ZSM-5 (Si/Al = 23), $\mathrm{WHSV_{methanol}} = 4.75\ \mathrm{h^{-1}}$, $\mathrm{P_{methanol}} = 1.4$ MPa, isooctane/methanol = 3 (molar ratio; SC study only)

The liquid hydrocarbon distributions for the SC MTH temperature studies are shown below in Figure 3.12. Over the course of the 300°C study, the relative amount of C9+ hydrocarbons remained stable at 27%, with the percentage of C3-C6 species decreasing only moderately with time on stream, from 47% at 4h to 38% at 50h. Both the initial and final product distributions differed greatly from those obtained under gas phase conditions. Greater carbon number diversity was observed even at 4h TOS in SC MTH compared with GP MTH. Furthermore, the pronounced shift toward C9+ species, which is symptomatic of catalyst aging and clearly observable from the results of the GP MTH study, was conspicuously absent from the SC MTH product distribution at 300°C. At a temperature of 370°C, only a 2% increase in the percentage yield of C9+ species was observed between 4h and 50h, while the relative amount of C6-C9 species decreased from 22% to 8%. This decrease in C6-C9 hydrocarbons and corresponding increase in C3-C6 hydrocarbons with TOS is an opposite trend from that observed for GP MTH at 370°C. Regardless of reaction temperature, the product distributions obtained under SC MTH conditions show greater uniformity with TOS compared to the GP MTH distributions. This suggests that the SC MTH reaction environment promotes more stable catalytic performance than the traditional gas phase operating conditions.

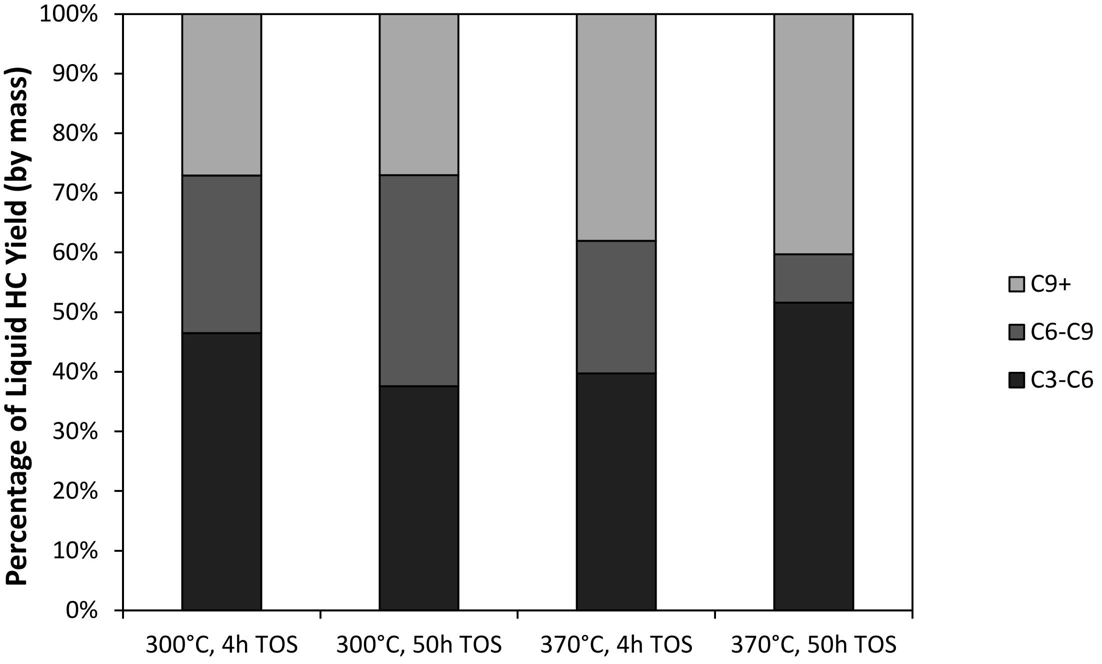

Figure 3.12 Supercritical isooctane phase hydrocarbon product distribution in the top liquid phase. Reaction conditions were as follows: catalyst = H-ZSM-5 (Si/Al = 23), $\text{WHSV}_{\text{methanol}}$ = 4.75 h^{-1}, P_{methanol} = 1.4 MPa, isooctane/methanol = 3 (molar ratio; SC study only)

3.3.2 Post-reaction Characterization of MTH Catalyst

Four MTH studies were carried out each using 1g of H-ZSM-5 exposed to 0.1 mL/min methanol flow at an approximate methanol partial pressure of 1.4 MPa. Two sets of studies, gas phase and SC isooctane phase, were each conducted for reaction temperatures of 300°C and 370°C. Following reaction, the coked catalyst samples were removed from the fixed-bed reactor and analyzed using N_2 physisorption (BET), XRD, and TGA.

3.3.2.1 N_2 Physisorption (BET)

The results of physisorption analysis are shown below in Table 3.1. The BET surface area, micropore area, total pore volume, and micropore volume of the fresh H-ZSM-5 are consistent with that previously observed for low silica H-ZSM-5 (Bjørgen et al., 2008). Compared to unused H-ZSM-5, all post-reaction catalyst showed a considerable decrease in surface area and pore volume as well as an increase in BET pore width. Catalyst samples retrieved after reaction at 370°C retained significantly more surface area and pore volume than samples retrieved after reaction at 300°C. The reduced surface area and pore volume of the lower temperature samples is most likely the result of coke location rather than an overall increase in coke content. While coke deposition is accelerated at higher temperatures (Benito et al., 1996), there is a thermodynamic preference for heavy product formation at lower temperatures (Chang et al., 1978; Froment et al., 1992). The suppression of secondary reactions such as cracking (Froment et al., 1992; Hutchings & Hunter, 1990) could hinder heavy product removal from catalyst active sites, resulting in increased blockage of zeolite microchannels at lower reaction temperatures. Table 3.1 shows a 3-4 fold reduction in catalyst micropore area and volume after reaction 300°C compared to reaction at 370°C.

Table 3.1 Catalyst pore and surface characteristics for used and unused H-ZSM-5

	H-ZSM-5 (unused)	GP MTH catalyst (370°C)*	SC MTH catalyst (370°C)	GP MTH catalyst (300°C)*	SC MTH catalyst (300°C)
BET surface area (m^2/g)	328.81	54.40	61.69	21.85	28.14
Micropore area (m^2/g)	287.23	42.6	47.0	11.1	13.3
Total pore volume (cm^3/g)	0.21	0.04	0.06	0.04	0.05
Micropore volume (cm^3/g)	0.15	0.02	0.03	0.006	0.007
BET pore width (nm)	2.60	3.20	3.58	7.34	7.75

*Low pressure ($P/P_0<0.4$) hysteresis observed in isotherm

Comparing GP and SC MTH catalysts from reaction at 370°C, the SC MTH catalyst exhibited higher surface area as well as higher pore volume, which indicates that the presence of the SC isooctane helped to improve catalyst maintenance under MTH reaction conditions. This could be accomplished by solvation and extraction of coke precursors from the internal zeolite channels or by reduced coke accumulation due to improved heat management in the presence of supercritical isooctane.

The physisorption results for SC MTH at 300°C also reflect better catalyst maintenance compared to GP MTH at the same temperature. As with the results for SC MTH at 370°C, surface area and pore volume were both higher for catalyst subjected to reaction at 300°C in the presence of SC isooctane. It is important to note that only the top 2/3, or most heavily coked, portion of the GP MTH catalyst bed was analyzed by N_2 physisorption. The catalyst retrieved after gas phase reaction displayed a slight color gradient which indicates that coking varied along the length of the catalyst bed (darkest at top, lightest at bottom). The coked catalyst retrieved after SC MTH, on the other hand, was both lighter and more homogeneous in color than the GP MTH catalyst. This suggests that coke laydown was more uniform across the catalyst bed under SC MTH conditions.

As Table 3.1 shows, BET pore widening relative to fresh H-ZSM-5 occurred in all samples exposed to MTH reaction conditions; however, pore widening of the catalyst was most extreme following reaction at 300°C. Increased pore widening suggests an increase in the ratio of mesopores to micropores within the post-reaction catalyst. All catalyst samples, including fresh H-ZSM-5, showed evidence of mesoporous structure, as indicated by the presence of a hysteresis loop between the adsorption and desorption isotherms (Figure 3.13a-c, shown below). This hysteresis loop is the result of capillary condensation of N_2, which occurs within mesopores (pores greater than about 2nm in size) (Sing et al., 1985). The hysteresis loop is much more pronounced in the isotherms of the catalyst from MTH at 300°C. Widening of the hysteresis loop is associated with increased mesopore formation (Bjørgen et al., 2008; van Donk, Janssen, Bitter, & de Jong, 2003).

Hydrothermal effects, such as dealumination or solvation, could account for pore widening and increased mesopore presence in the post-reaction catalyst samples. A substantial amount of water is produced in the dehydration of methanol and DME to hydrocarbons. At the MTH conditions studied, this water should exist as superheated steam. One of the most common methods of inducing mesopore formation in zeolites is through the removal of framework aluminum atoms by steaming (van Donk et al., 2003). Even moderate levels of dealumination (<30%) have been shown to result in the formation of secondary mesopores (Zukal & Patzelova, 1986). For Y zeolite, it has also been observed that, at 200°C compared to 300°C, steam has a stronger decomposition effect on crystal structure, possibly owing not to increased dealumination, but to the stronger solvation effect of low temperature water on the zeolite framework itself (Salman et al., 2006). Thus, for the used MTH catalyst, the significant reduction in micropore volume and the increase in pore width at 300°C compared to 370°C could be due, at least in part, to temperature effects on the physical properties of steam.

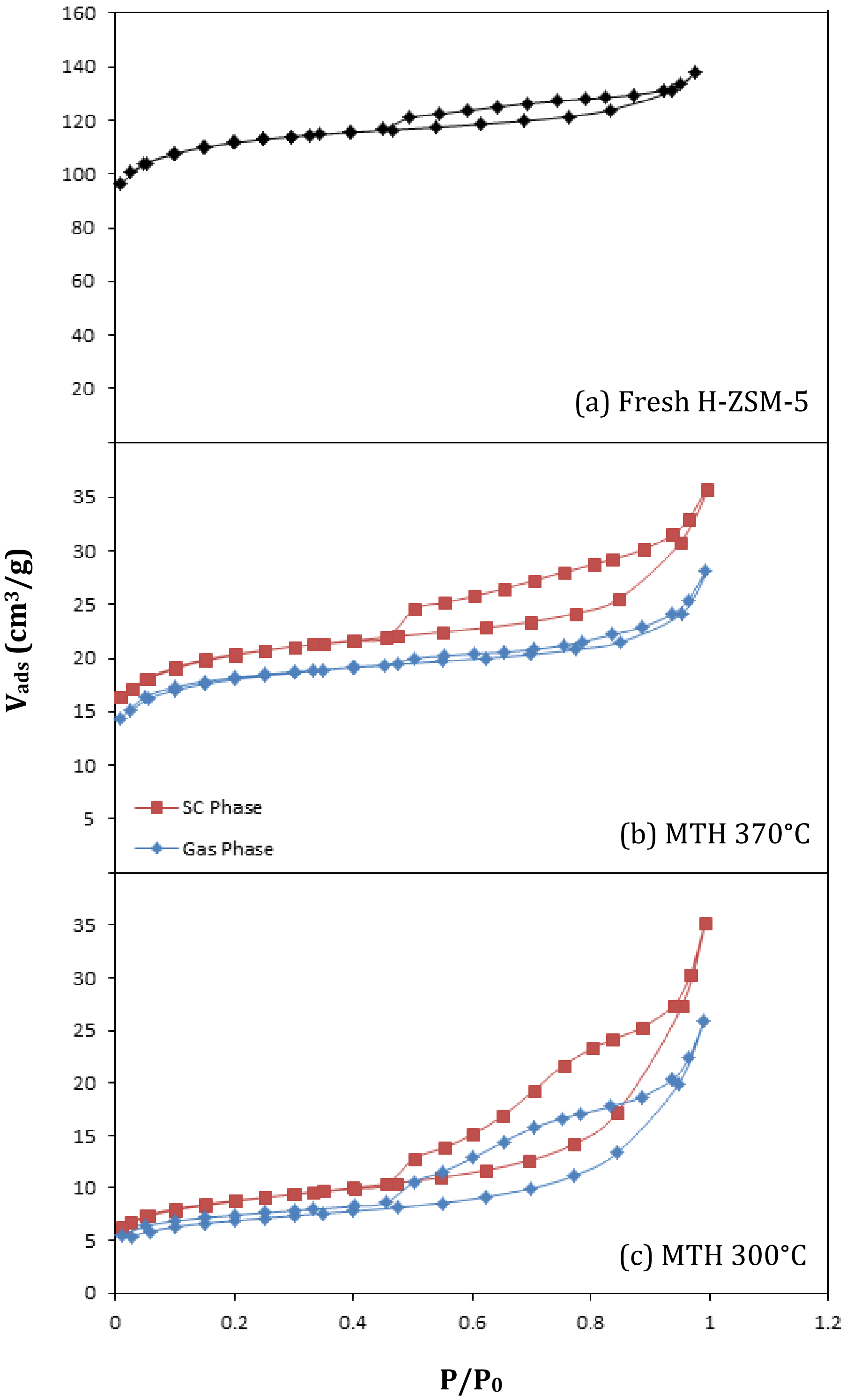

Figure 3.13 Isotherms of N_2 adsorption and desorption for (a) unused H-ZSM-5 (b) H-ZSM-5 after MTH at 370°C (c) H-ZSM-5 after MTH at 300°C

Comparing the SC MTH and GP MTH isotherms in Figure 3.13, it is apparent that the supercritical reaction environment has an effect on the hysteresis patterns observed in the post-reaction catalyst isotherms. This effect is most pronounced in Figure 3.13b, which compares the isotherms of MTH catalysts retrieved after reaction at 370°C. In Figure 3.13b, the relative collapse of the hysteresis loop in the GP MTH isotherm suggests that blockage of mesopores was more severe than under SC MTH conditions, where the hysteresis loop is more distinct and the total pore volume of the catalyst is significantly higher. Additionally, the low pressure hysteresis observed in the GP MTH isotherms of Figure 3.13b and c suggests that the desorption of N_2 was affected by swelling of coked zeolite channels and/or the presence of coke which could restrict pore dimensions. Low pressure hysteresis ($P/P_0<0.4$) can result from the swelling of non-rigid pores or from the irreversible sorption of adsorbate, either through chemical interaction with the adsorbent or through inability of the adsorbate to escape through restricted pores (Sing et al., 1985). As shown in Figure 3.13, the isotherms of the SC MTH catalyst, like that of fresh H-ZSM-5, do not show evidence of this low-pressure hysteresis, suggesting that the pore channels are less restricted by the presence of internal coke.

3.3.2.2 Powder X-Ray Diffraction (XRD)

A portion of the XRD spectra obtained for both unused and post-reaction catalyst is shown below in Figure 3.14. All five spectra in Figure 3.14 exhibit the characteristic XRD pattern of ZSM-5, as found in the literature (Wu, Lawton, Olson, Rohrman, & Kokotailo, 1979). Since the particles of the catalyst samples were sieved to 45-70 mesh, particle size effects, which could cause changes in crystallinity (Al-dughaither & Lasa, 2014), are not expected to contribute significantly to the differences observed among the various XRD spectra. The XRD pattern of unused H-ZSM-5 (spectrum (a) in Figure 3.14), with a Si/Al ratio of 23 to 1, is consistent with that previously reported for H-ZSM-5 with low Si/Al ratio (30:1) (Al-dughaither & Lasa, 2014).

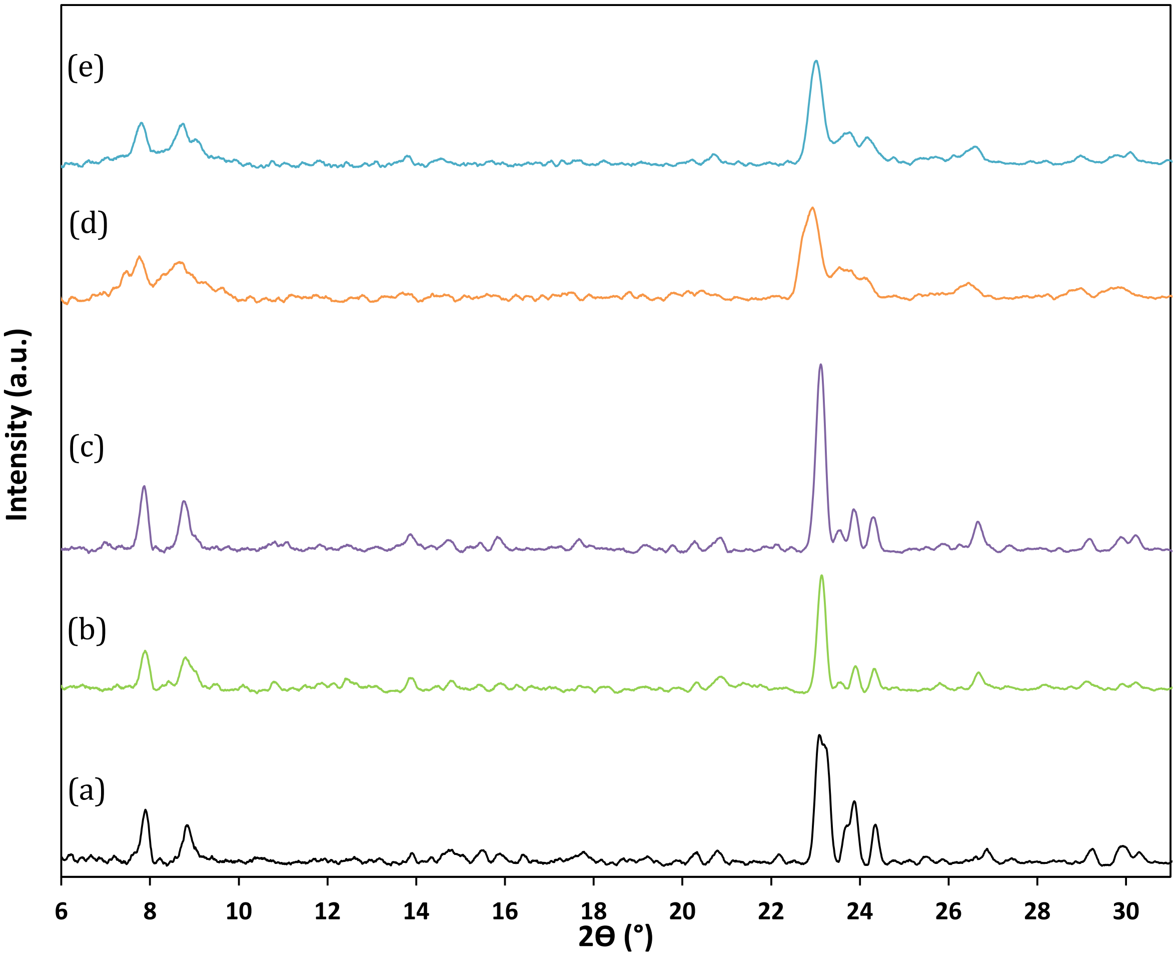

Figure 3.14 XRD spectra of (a) unused H-ZSM-5 and H-ZSM-5 from (b) SC MTH at 370°C (c) GP MTH at 370°C (d) GP MTH at 300°C (e) SC MTH at 300°C

The most notable changes between the unused and post-reaction catalyst in Figure 3.14 occur in the 23° to 25° 2*θ* range. Compared to unused H-ZSM-5 (spectrum (a) in Figure 3.14), all catalyst samples retrieved after MTH reaction show a transition from doublet peak to singlet peak at 23.1° 2*θ*. The shift from doublet to singlet peaks in the XRD patterns of used vs. unused H-ZSM-5 in Figure 3.14 indicates a change in the crystal symmetry of the catalyst. It is known that the presence of organic material in the zeolite framework can affect changes in the crystal symmetry of ZSM-5 (Bibby et al., 1986; Fyfe, Kennedy, Schutter, & Kokotailo, 1984; Uguina, Serrano, Grieken, & Venes, 1993; Wu et al., 1979). Doublet peaks are indicative of monoclinic symmetry, while singlet peaks indicate orthorhombic symmetry. The presence of monoclinic vs. orthorhombic symmetry is the result of minor displacements in the atomic arrangement of the zeolite framework (Wu et al., 1979).

After reaction at 370°C, SC and GP MTH catalyst samples (spectrums (b) and (c) in Figure 3.14, respectively) show an increase in the relative intensity of the singlet peak at 23.1° 2θ as well as a transition from doublet peak at 23.8° 2θ to two singlet peaks at 23.4° and 23.85° 2θ. Changes in peak patterns between 23° and 25° 2θ are brought about by the different types of molecules sorbed within the zeolite, which alter the dimensions of the unit cell (Fyfe et al., 1984). For the GP and SC MTH catalyst samples, the observed pattern in the 23° to 25° range is consistent with that previously reported for internally coked H-ZSM-5 (Bibby et al., 1986; Uguina et al., 1993). Increasing the coke concentration from 0.85% to 23% has been previously associated with elongation of the peak at 23.1° 2θ as well as emergence of the single peak at 23.4° 2θ (Bibby et al., 1986), both of which are consistent with the XRD results obtained for the above GP and SC MTH catalyst. In particular, the relative increase in the 23.1° peak for GP compared to SC MTH suggests an increase in coke accumulation within the catalyst pores. Additionally, the decrease in the SC MTH low angle peaks is consistent with the effects of pore filling previously described (Fyfe et al., 1984).

The SC and GP MTH catalyst samples retrieved after reaction at 300°C (Figure 3.14 spectrums (e) and (d), respectively) appear to exhibit a loss of overall peak sharpness and definition in the 23° to 25° 2θ-range, compared to fresh H-ZSM-5. The broadening and coalescence of peaks in this 2θ-range could be the result of structural changes due to the amorphizing effects of steam. At lower temperatures, steam may have a stronger solvation effect on the zeolite framework (Salman et al., 2006), and exposure to steam can lead to destruction of the crystal lattice through the formation of secondary porous structures (Zukal & Patzelova, 1986).

3.3.2.3 Thermogravimetric Analysis (TGA)

The TGA results for both fresh H-ZSM-5 and post-reaction catalyst are shown below in Figure 3.15 as a function of time. Weight loss before 50 minutes time-on-stream is attributed to the desorption of water. Subsequent weight loss after 50 minutes is the result of coke burn-off, which has been previously observed starting at around 380°C (Liu, Li, Tian, & Xu, 2001).

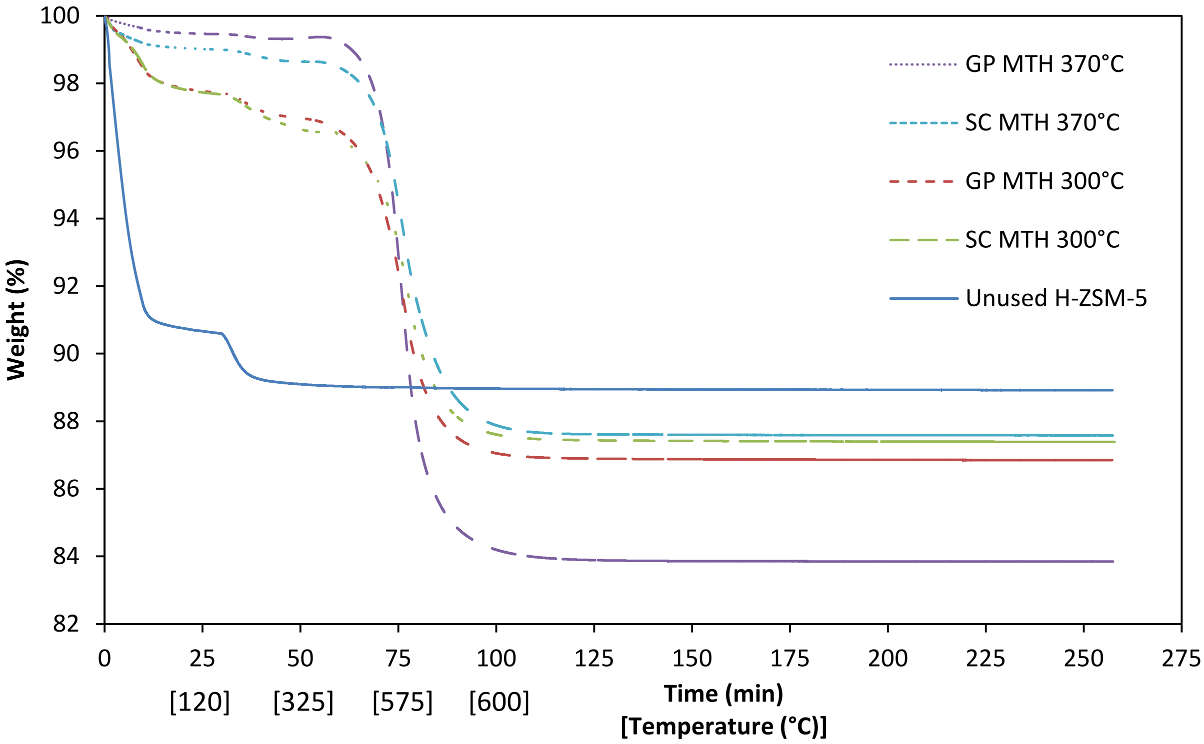

Figure 3.15 TGA profiles for unused H-ZSM-5 and post-reaction catalyst as a function of time

As can be seen from Figure 3.15, fresh or unused H-ZSM-5 has a high capacity for water adsorption, which accounts for about 11% of sample weight. After reaction, the capacity for water sorption appears to decrease relative to fresh H-ZSM-5. This is most likely due to the blockage of catalyst acid sites by coke molecules, which could hinder water adsorption. Previous studies have shown a decrease in H-ZSM-5 acidity with increasing coke content (Benito et al., 1996). At 370°C, the SC MTH catalyst demonstrates a greater capacity for water sorption compared to the GP MTH catalyst. The water desorption profiles of the SC and GP MTH catalyst samples at 300°C are almost identical and both show a much sharper decline than that of the 370°C post-reaction catalyst, indicating a greater capacity for water retention at 300°C.

The amounts of water and coke retained on the catalyst samples are presented below in Table 3.2. Both water and coke content were determined relative to the catalyst mass from TGA at 150 min TOS.

Table 3.2 Water and coke content of catalyst samples

	H-ZSM-5 (unused)	**GP MTH catalyst (370°C)**	**SC MTH catalyst (370°C)**	**GP MTH catalyst (300°C)**	**SC MTH catalyst (300°C)**
Water Content (wt %)	12.25%	0.79%	1.55%	3.49%	3.86%
Coke Content (wt %)	–	18.44%	12.60%	11.61%	10.55%

From Figure 3.15 and Table 3.2, it is clear that under SC MTH conditions less coke is retained on the post-reaction catalyst samples. This is most likely due to the ability of the SC isooctane to extract coke and/or coke precursor molecules from the mesopores and external surface of the H-ZSM-5 catalyst. With regards to coking, the ameliorating effect of the supercritical reaction environment was most pronounced for catalyst exposed to MTH reaction at 370°C. After reaction at 370°C, the GP MTH catalyst contained nearly 6% more coke than the SC MTH catalyst. Regardless of reaction environment, greater coke content was observed at 370°C than at 300°C. Coke accumulation is known to be more severe at higher reaction temperatures (Benito et al., 1996). Following reaction at 300°C, the difference in coke content between GP and SC MTH was only about 1% less under SC MTH conditions. This suggests that the coke removal benefits of the SCF medium are relatively lower at reduced reaction temperatures, most likely as a result of the restricted diffusion of isooctane in the microchannels of H-ZSM-5 (Choudhary & Choudhary, 1997).

3.4 Conclusion

In this chapter, the effect of a supercritical isooctane reaction medium on MTH reaction performance and catalyst maintenance was investigated at 300°C and 370°C. At 300°C, conversion of methanol remained relatively stable over the course of the 50-h study, with DME being the primary product at this low MTH reaction temperature. Compared to gas phase operation at 300°C, the presence of the SCF medium appears to have had no adverse effect on catalytic activity, as evidenced by high and stable methanol conversion with TOS under SC MTH conditions. At 300°C, higher carbon selectivity toward vapor phase hydrocarbons as well as higher liquid hydrocarbon yields were attained by conducting the reaction in a supercritical rather than a gas phase environment. The reaction performance for both GP and SC MTH at 370°C differed dramatically from the performance at 300°C, with both liquid and vapor hydrocarbon production elevated at this more typical MTH reaction temperature. A steady but gradual decline in methanol conversion was observed under SC MTH operation, while methanol conversion in GP MTH remained higher but showed an abrupt decline after about 24h TOS. Between 24h and 50h TOS, vapor hydrocarbon selectivity and liquid hydrocarbon yield in GP MTH began to decline relative to hydrocarbon production in SC MTH, with an increasing amount of converted methanol going to DME in GP MTH. At both 300°C and 370°C, a considerable shift toward the production of C9+ hydrocarbons was observed between 4h and 50h TOS in GP MTH, while in SC MTH the product distribution at both reaction temperatures remained relatively stable with TOS. Furthermore, for both 300°C and 370°C, catalyst surface area and pore volume following SC MTH reaction exceeded the area and volume retained after GP MTH operation. The fact that retained surface area and pore volume was less following reaction at 300°C compared with reaction at 370C° is most likely the result of a difference in the location of coke rather than a higher amount of coke at this lower reaction temperature. XRD results revealed a more pronounced pattern of internal coking at 370°C compared to 300°C, further suggesting that the mode of catalyst deactivation at 300°C is external coking. Oxidation of the post-reaction catalyst showed higher coke content of GP MTH catalyst compared to SC MTH catalyst, with coking being most severe under GP MTH conditions at 370°C. More stable reaction performance with TOS coupled with higher retained surface area and pore volume and reduced coke content indicate that operation of the MTH reaction in the presence of supercritical isooctane promotes more stable catalytic performance.

Chapter 4 Future Work

4.1 Effect of Operating Variables on SCF-assisted MTH

Chapter 3 explored the effects of reaction temperature and reaction environment (gas phase vs. SC isooctane phase) on the performance of the MTH reaction carried out over catalyst H-ZSM-5. It is clear from the results presented in Chapter 3 that both the temperature and the reaction environment had a dramatic impact on catalytic performance. Regardless of reaction environment, raising the reaction temperature from 300°C to 370°C resulted in an increase in overall liquid hydrocarbon production and a steeper decline in methanol conversion with TOS. Increased conversion to hydrocarbon species at elevated reaction temperatures has been previously reported in the literature (Chang et al., 1978), as well as a rapid decline in methanol/DME conversion at 370°C (Bjørgen et al., 2008). Compared with gas phase operation at the same temperature, operating the reaction in the presence of supercritical isooctane (molar ratio of SC isooctane/methanol = 3) resulted in increased liquid hydrocarbon production with TOS, a more uniform hydrocarbon product distribution with TOS, and improved catalyst maintenance, as observed in the post-reaction analysis of catalyst samples. This more stable catalytic performance under supercritical conditions has also been observed for other reactions, including FTS (Nimir O Elbashir et al., 2010).

The benefits of supercritical operation in the MTH reaction depend strongly on the reaction temperature. At 300°C, consistently higher reactant conversion and hydrocarbon production were achieved under supercritical reaction conditions compared to gas phase; however, the overall yield of liquid hydrocarbons was much greater at 370°C than at 300°C. Furthermore, the ameliorating effect of the SC environment on catalyst coking was more pronounced at 370°C than at 300°C. Nearly 6% less coke by weight was retained under SC MTH conditions at 370°C, while at 300°C only 1% less coke was retained under SC isooctane conditions compared to GP conditions. These observations suggest there may be an optimal temperature in the range of 300°C to 370°C at which the supercritical fluid may be beneficial for both reaction performance and catalyst maintenance. Future temperature studies would be useful to determine the best operating temperature to achieve higher hydrocarbon yields while maintaining stable catalytic performance.

More studies are also needed to determine an optimal value for SC isooctane to methanol molar ratio (i.e., media ratio). A media ratio of 3 was chosen for the investigations reported in Chapter 3 based off previous application of supercritical solvents in other reactive systems such as FTS and HAS, where molar ratios of SCF/reactant typically range from 3 to 3.5 (E. Durham et al., 2010; Xu et al., 2013). Above a molar ratio of around 3, lower FTS catalyst activity and higher required operating pressure were found to outweigh the selectivity benefits of increased SCF presence (N. O. Elbashir, Dutta, Manivannan, Seehra, & Roberts, 2005). While MTH shares some similarities with FTS and HAS (i.e., large heat of reaction and mass transfer limitations), MTH chemistry and conditions differ substantially from that of FTS and HAS. Because of the differences in catalyst type and operating conditions, the optimal value for molar ratio of SCF to reactant in MTH may vary considerably from that found for FTS and HAS. It is possible that less solvent could be utilized to achieve similar benefits in reaction performance and catalyst maintenance to those observed in Chapter 3 for a molar ratio of 3 to 1 isooctane to methanol.

Another process variable that should be investigated is system pressure. While the effects of methanol partial pressure on MTH have been previously studied (Chang et al., 1979), the effect of total pressure on reaction performance is largely unknown. As mentioned previously, employing a SCF reaction medium necessitates higher operating pressure in order to maintain constant reactant partial pressure. Thus, it is possible that some of the effects observed in the presence of SC isooctane in Chapter 3 could be due to the thermodynamic pressure effect on the reaction rate constant. In order to decouple the effects of supercritical fluid amount and system pressure, an inert balancing gas could be used to increase the system pressure while maintaining constant pressure and constant SCF to methanol ratio. This would allow for the effects of system pressure on MTH performance under both gas phase and SC isooctane phase conditions to be isolated. A similar balancing gas study was undertaken to isolate SC solvent effect in HAS (Xu et al., 2013). Additionally, the physical properties of the SCF medium itself vary considerably with changes in pressure (Baiker, 1999). Increasing the system pressure would increase the supercritical solvent density and thermal conductivity which could have interesting consequences for product/coke extraction and heat removal.

4.2 Investigation of Alternative SCF Media

In the SC MTH investigations presented in Chapter 3, isooctane (2,2,4-trimethylpentane) was selected as the SCF reaction medium primarily because of its low reported reactivity over H-ZSM-5: 0.3% at 400°C and ambient pressure (Akolekar, 1993). Under the high-pressure reaction conditions described in Chapter 3, less than 1% isooctane conversion was observed at 300°C, with less than 5% conversion observed at 370°C. High solvent reactivity is associated with accelerated catalytic deactivation, as discussed below. The low reactivity of isooctane is attributed to its highly bulky structure, which inhibits diffusion in the H-ZSM-5 pore channels (Choudhary & Choudhary, 1997) and/or adsorption of isooctane at the H-ZSM-5 active sites (Denayer et al., 1998).

Restricted diffusion of isooctane in the H-ZSM-5 microchannels may limit its usefulness as an SCF medium in the MTH reaction. Because of its high critical temperature (271°C) and low critical pressure (26 bar), supercritical isooctane's properties under the MTH reaction conditions are more liquid-like than gas-like: estimated density = 0.37 g/mL at 300°C and 7.2 MPa (Baled et al., 2012). As a dense, more liquid-like medium, isooctane is well-suited for heat removal, but the hindered diffusivity of the isooctane molecules in the catalyst pore system may restrict the mass transfer benefits of the SCF medium to the external catalyst surface only.

Smaller hydrocarbon species, which can more readily traverse the H-ZSM-5 micropores, could better facilitate coke and/or product extraction capabilities than isooctane. Although the supercritical properties of lower carbon solvents such as n-pentane would be more gas-like under MTH conditions due to their comparably lower critical temperatures, they are still capable of creating a more dense reaction environment than gaseous methanol alone. The estimated densities of methanol compared to C4-C6 supercritical solvents at the same MTH conditions are presented below in Figure 4.1.

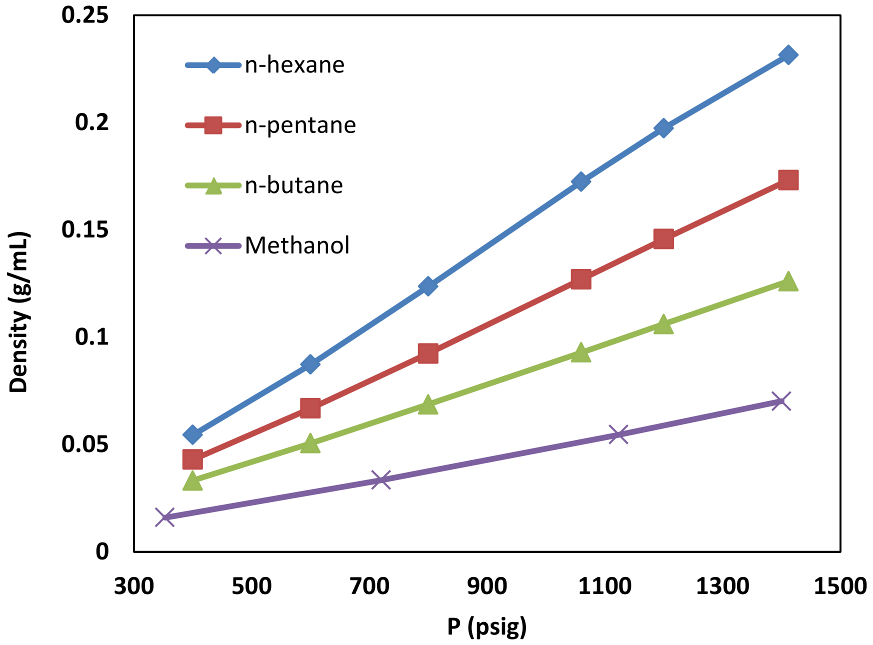

Figure 4.1 Supercritical hydrocarbon solvent density vs. methanol density at 370°C. Densities estimated using the Peng-Robinson equation of state

Preliminary investigations carried out with supercritical n-pentane under similar reaction conditions as those described in Chapter 3 for the SC isooctane studies have revealed significant conversion of n-pentane to vapor and liquid hydrocarbon species. Even at a reaction temperature as low as 300°C, over 30% n-pentane conversion was observed. Following the introduction of methanol to the SC n-pentane and H-ZSM-5 catalytic system, rapid catalytic deactivation occurred, with methanol conversion dropping from 94% to 34% in less than 12h TOS. Because this deactivating effect was not observed in the presence of SC isooctane, the adverse effect of the SC pentane environment on methanol conversion is attributed to the high reactivity of the solvent.

Although n-pentane is not ideal for use as an SCF medium in MTH, other small-chain species such as n-butane may still be useful as solvents in this reaction. Hydrocarbon adsorption in H-ZSM-5 decreases significantly with decreased carbon number and increased chain branching (Denayer et al., 1998). With these considerations in mind, a possible SCF candidate for the MTH reaction is isobutane, which should have low reactivity due to its low carbon number and highly branched structure. A historical precedent for this investigation can be found in the original Mobil MTG reaction scheme, in which a sub-critical stream of recycled C3 and C4 hydrocarbons was fed to the conversion reactor to provide heat transfer benefits and ameliorate the MTG product distribution (Chang et al., 1978). It is reasonable from a commercial standpoint, therefore, to investigate the application of supercritical C4 hydrocarbons with the aim of further improving MTH reaction performance.

4.3 Application of SCF Media to Alternative MTH Catalytic Systems

All supercritical MTH studies in Chapter 3 were carried out over the zeolite catalyst H-ZSM-5, which has been widely investigated in the conversion of methanol to gasoline. While H-ZSM-5 is the most common MTH catalyst, it may not be the most well-suited for supercritical operation. Medium-pore zeolites such as H-ZSM-5 show a relatively low coking tendency, which is attributed to transition state selectivity (Froment et al., 1992).

Larger pore catalysts such as zeolite Y, which can deactivate rapidly due to coke accumulation (Froment et al., 1992), may benefit more from the application of a SCF reaction medium. In the disproportionation of ethylbenzene over various zeolite catalysts, application of supercritical n-pentane showed the most coke reduction benefit in the zeolite Y system, with only modest benefits observed over H-ZSM-5 (Niu & Hofmann, 1996). Larger and bulkier hydrocarbon solvents such as isooctane would have increased accessibility and therefore greater product/coke extraction capability in large pore catalytic systems. Depending on the pore structure and acidity of the catalyst, however, branched hydrocarbons could actually have greater reactivity than straight chain hydrocarbons. For large-pore catalyst SAPO-5, n-hexane conversion was 0.8% lower than that of isooctane at 400°C (Akolekar, 1993). Thus, the ideal SCF for a given large-pore MTH catalytic system may vary, but in general, long chain hydrocarbon solvents with critical points better suited to MTH conditions should be applicable in these systems.

Potential also exists for SCFs to benefit MTH carried out over small-pore catalysts. As described in Chapter 1, small-pore molecular sieve SAPO-34 is a highly effective catalyst in the conversion of methanol to light olefins (Stocker, 1999). The microporous openings of SAPO-34 prevent the diffusion of branched and aromatic hydrocarbons, which leads to rapid coke accumulation within the cage-like structure of the catalyst (D. Chen, Moljord, Fuglerud, & Holmen, 1999). In addition to facilitating heat and external coke extraction, the application of a small-chain (C3 or C4) SCF has the potential to mitigate internal coking as well, by extracting reaction products before they aromatize to form coke. As with solvent selection in large and medium pore catalytic systems, selection of the appropriate SCF for use in small-pore MTH catalysts will depend on the exact pore structure of the catalyst in question.

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