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Addition of Zeolite ZSM-5 to an Iron-based Fischer-Tropsch Catalyst supported on Activated Carbon: Effect of Reactor Conditions

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Addition of Zeolite ZSM-5 to an Iron-based Fischer-Tropsch Catalyst supported on Activated Carbon: Effect of Reactor Conditions

Avinashkumar V. Karre

**Thesis Submitted to the College of Engineering and Mineral Resources
at West Virginia University
in partial fulfillment of the requirements
for the degree of**

**Master of Science
in
Chemical Engineering**

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Morgantown, West Virginia

2011

Keywords: Fischer-Tropsch; Iron-based catalyst; ZSM-5; activated carbon

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ABSTRACT

Addition of Zeolite ZSM-5 to an Iron-based Fischer-Tropsch Catalyst supported on Activated Carbon: Effect of Reactor Conditions

Avinashkumar V. Karre

An iron-based catalyst containing 6 wt% Mo, 16 wt% Fe, 0.8 wt% Cu, and 0.9 wt% K supported on Norit SX Ultra activated carbon is used as a FTS catalyst. Zeolite ZSM-5 (of medium acidity and Si/Al = 50) is used to check its effect on FT base catalyst to form aromatic compounds and to reduce the size of long-chain hydrocarbons. The influence of ZSM-5 amounts, bed arrangements, and the temperature on the product distribution were investigated.

The performance of ZSM-5 along with the base catalyst was analyzed in two catalyst bed configurations: separate-bed and mixed-bed. Both separate-bed and mixed-bed catalyst arrangements show conversion of alcohols to hydrocarbons and water. The separate-bed arrangement gives higher conversions of CO and H₂, and higher yields of liquid hydrocarbons. The decline in FT activity in the mixed bed is probably due to lowering of the alkali content of the iron catalyst because of alkali migration from FT catalyst to ZSM-5, as confirmed by energy-dispersive X-ray spectroscopy of the spent ZSM-5.

Product profiles were analyzed for changing ZSM-5 weight from 50 to 200 % of the FTS amount in the separate bed and the mixed bed catalyst arrangements. Oligomerization, aromatization, isomerization, and cracking reactions are enhanced with increasing ZSM-5 weight in both the catalyst arrangements. The base catalyst shows no selectivity towards aromatic compounds, but addition of ZSM-5 in both arrangements forms C₇₋₁₀ aromatic compounds. Long-chain hydrocarbon molecules (C₁₃₊) formed by the base catalyst are effectively cracked, and isomerized on the ZSM-5 catalyst surface in both type of catalyst arrangements.

Product profiles were analyzed for change in the temperature from 280 to 320°C in the base catalyst as well as in the separate-bed catalyst arrangement. Amounts of small-chain hydrocarbons (C₁₋₅) increase with increase in temperature because of higher FTS rates. Liquid hydrocarbon production rate (in both the base catalyst and the separate bed) is increased at 300°C due to increase in FTS rate. Further increase in the temperature causes these rates to drop to give small-chain hydrocarbon (C₁₋₄) species. Aromatic yields are found to reach a maximum at 300°C in the separate bed. The alcohol rate for the base catalyst increases with increase in temperatures probably because of higher FTS rates. 280°C is sufficient to convert all the alcohols formed by the base catalyst in the separate bed.

The base catalyst and ZSM-5 together were tested for 240 h time on stream (TOS) to check the stability of the combination of the catalysts in the separate-bed arrangement. The base catalyst shows stability up to 120 h and slow decline in activity up to 240 h. A progressive loss of the ZSM-5 activity occurred with TOS. Coke deposition on ZSM-5, confirmed by energy-dispersive X-ray spectroscopy, decreases aromatic compound yield, and increases olefin selectivity with time on stream due to reduction in oligomerization reactions.

Dedicated to my family

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CHAPTER 1

INTRODUCTION

The world's fuel need is predominantly dependent on crude oil (Dry, 2002). Oil prices are rising continuously since 1960. Oil reserves are also limited and the demand for fuel is increasing day by day. The negative effect of oil prices on the economy is significant, and should be used to build the business case to invest in alternative energy like coal, methane, and renewable energy (Owen et al., 2010).

Presently known reserves of methane and of coal exceed that of crude oil by factors of about 1.5 and 25 respectively (Dry, 2002). Therefore, production of syngas from methane or coal and conversion of the syngas to a range of fuels and chemicals could be of interest (Dry, 2002). For all these reasons, the Fischer-Tropsch (FT) process is an ideal candidate to fulfill the energy demands. Development should be in areas that decrease the capital costs of use of syngas through the FT process and improve the thermal efficiency of the plant as a whole (Vasloo, 2001).

Application of FT involves complex integrated plants. The plant consists of synthesis gas preparation, FT synthesis and product upgrading. Some advantages of FT hydrocarbons, compared to crude oil, as a feedstock for fuel production are the absence of sulfur, nitrogen or heavy metals, and the low aromatic content (Forghani et al., 2009). The kerosene produced has good combustion properties and high smoke points, and the diesel fuel produced has a high cetane number and can be used in blending purposes (Steynberg, 1999).

Martinez et al. (2005) showed that the chain size of constituents of the FT liquid can be limited beyond the gasoline-range product with the addition of ZSM-5 to form dual-functional FT catalyst. Thus the pore structure of ZSM-5 and its catalytic cracking active sites can limit the size of produced molecules (Pour et al., 2008).

1.1 FISCHER-TROPSCH PROCESS

The FT process is a key component of gas-to-liquids (GTL) technology, producing a petroleum substitute, typically from coal, natural gas, or biomass. The FT process is a set of chemical reactions that convert a mixture of carbon monoxide and hydrogen into liquid hydrocarbons. The chemical reactions lead to a series of both desirable products and undesirable byproducts and the

liberation of a large amount of heat from the highly exothermic synthesis reactions (Stenger et al., 1986; Espinoza et al., 1998; Steynberg et al., 1999). The FT products are olefins, oxygenates, gasoline-, diesel-, and kerosene-range paraffins. The products gasoline- and diesel-range paraffins are desirable because these products are already established and proven in the market. Moreover, this project details are mainly concerned on these products. Useful reactions that give alkanes $C_nH_{(2n+2)}$, where 'n' is a positive integer, are generalized as (Luo et al., 2009):

The water-gas-shift reaction (WGS) also occurs in FT process. WGS is expressed as:

Generally, the FT process is operated in the temperature range of 150–300°C. Higher temperatures lead to faster reactions and higher conversion rates, but also tend to favor methane production (Schulz et al., 1991). As a result, the temperature is usually maintained in the low to middle part of the range. Increasing the pressure leads to higher conversion rates and also favors formation of long-chain alkanes. Typical pressures range from one to several tens of atmospheres. Even higher pressures would be favorable, but the benefits may not justify the additional costs of high-pressure equipment (Schulz, 2003).

A variety of synthesis-gas compositions can be used. For cobalt-based catalysts, the optimal H_2 : CO ratio is around 1.8-2.1 (Dry, 2002). Iron-based catalysts promote the WGS reaction (Equation 1.2) and thus can tolerate significantly lower ratios. WGS can be important for synthesis gas derived from coal or biomass, which tend to have relatively low H_2 : CO ratios (< 1) (Lohitharn et al., 2008).

1.2 INTEREST IN FISCHER-TROPSCH PROCESS

Linear long-chain hydrocarbons usually dominate the FT products, which need post-cracking or isomerization to obtain transportation fuels like gasoline, diesel. The use of different zeolites in combination with a FT catalyst has been investigated by Botes et al. (2004). Vytnova et al. (2006) suggests the use of ZSM-5 in the cracking of the long-chain hydrocarbons. Note that zeolites are used in our experiments for FT liquid production. During recent years, the use of FT has gained lot of research interest. Some of the factors that contribute to interest in FT are:

- An increase in the known reserves of natural gas (Owen et al., 2010).

- Environmental pressures to minimize the flaring of associated gas (Waldner et al., 2001).

1.3 CHALLENGES IN FISCHER-TROPSCH PROCESS

The area of concern in FT plants should be to decrease the capital cost of syngas generation and to improve the thermal efficiency of the plant as a whole. The very common way of improving the thermal efficiency of the process is to combine the FT process with a power generation plant. Such a combination will create a more efficient use of the low-pressure steam produced by the FT process (Vosloo, 2001).

Also, in order to reduce the total cost of the catalyst in the FT process, an iron-based catalyst can be used. Note that an iron-based catalyst will be used in our experiments for FT liquid production.

1.4 COMMERCIAL FISCHER-TROPSCH PLANTS

There are many companies involved in Fischer Tropsch business. Some are shown in Table 1.1.

Table 1.1 Commercial Fischer-Tropsch plants

Company	Location	Size (BPD)	Type of Products	Year of Production Start	References
Sasol	South Africa	124,000	Light olefins and gasoline	1955	Dry (2001)
Moss Gas	South Africa	22,500	Gasoline and diesel	1991	Knottenbelt (2002)
Shell	Malaysia	20,000	Waxes, chemicals, diesel	1993	Vilet et al. (2009)

1.5 OBJECTIVE OF THIS STUDY

The idea here is to increase gasoline- and diesel-range hydrocarbons. The present research investigates this as follows:

- The high-silica ZSM-5 zeolite is evaluated in two process configurations. In one operating mode, Fe catalyst and ZSM-5 are placed in separate zones. In the other operating mode, the Fe catalyst and ZSM-5 are mixed. Here the effect of catalyst bed configuration is checked.
- The effects of reaction conditions (temperature, changes in ZSM-5 weights, TOS) are investigated, and the liquid and gas products formed are analyzed. These conditions are important to compare the iron-based catalyst with the dual-functional catalyst system (Fe-based + ZSM-5).

CHAPTER 2

LITERATURE REVIEW

The focus of the present research is on Fe-based catalysts because of their high water-gas-shift (WGS) activity in addition to their high FT activity. Fe-based catalysts are also low cost and have low selectivity towards methane (Li et al., 2007). In addition, introduction of zeolites into a FT catalyst increases cracking of heavier liquid hydrocarbons (Abramova et al., 2005), and this is also considered here.

2.1 OVERVIEW

FT synthesis mainly uses cobalt- (Co) and iron-based catalyst commercially (Yang et al., 2005). There are some disadvantages to using a Co-based catalyst. Cobalt is 1000 times more expensive as iron (Davis, 2003). Cobalt-based catalysts are only used in the Low-Temperature Fischer-Tropsch (LTFT) process, as excess methane is produced at the higher temperatures (Dry, 2002). The Fe-based FT catalyst is able to use low H₂/CO ratios of synthesis gas from coal gasification, whereas the Co-based FT catalyst needs a higher ratio (Wan et al., 2008).

FT synthesis suffers mainly from two problems. One is that polymerization leads to waxy products. Waxy products are long-chain hydrocarbons (Martinez et al., 2007). Hence, the chain length of hydrocarbons needs to be adjusted so that primary gasoline- and diesel-range products are formed (Ma et al., 2007b). Ma et al. (2007 b) have shown that the chain length of FT liquids could be controlled below C₂₀ over an activated carbon support. Martinez et al. (2007) used zeolite as a cracking catalyst and showed that FT liquids can be cracked to gasoline- and diesel-range products. Therefore we can use zeolite and activated carbon together for tailoring of product hydrocarbon.

2.2 REACTION INVOLVED IN THE FISCHER TROPSCH PROCESS

The chemistry in FT process is very complex but can be simplified into the following chemical reactions (Dry, 2004). Methane formation takes place as follows:

Heavier hydrocarbons form as follows:

Alcohols are produced by:

The FT process depends on the ratio of consumption of hydrogen and carbon monoxide. From Equation (2.2), this ratio is 2 for hydrocarbons. The WGS reaction, Equation (1.2), which essentially converts excess CO to H₂, is favored by the iron catalyst (Haijun et al., 2008). Hence, we can carry out the FT process using the Fe-based catalyst with feeds having the ratio of H₂ to CO ≤ 1 (Riedel et al., 1999). A cobalt-based catalyst favors Equation (2.1) which uses H₂ to form methane which is an unneeded product, hence the feed ratio of H₂ to CO in case of cobalt catalyst is typically between 2.06 to 2.16 (Dry, 2004).

2.3 KINETICS OF FISCHER-TROPSCH PROCESS

There are many rate models reported in the literature. Some are listed in Table 2.1.

2.4 REACTION MECHANISMS

The FT synthesis is a polymerization reaction in which monomers are produced from the reactants hydrogen and carbon monoxide. Hence, FT reactions can be divided into the following three sections (Claeys et al., 2004):

1. Generation of the chain initiator
2. Chain growth or propagation
3. Chain termination or desorption

There are several FT mechanisms reported in the literature described below. Here M is a metal, R is CH₃, etc.

Table 2.1 Iron-based kinetic rate models

Rate Model	Catalyst	T (°C)	k (mol/g-cat . h. MPa)	P (psi)	a,b or c	Reference	H ₂ /CO ratio
$r_{FT} = \frac{k P_{CO} P_{H_2}}{P_{CO} + a P_{H_2O}}$	CCI fused iron	250 282 315	0.0017 0.0049 0.013	NA	0.028 0.028 0.028	Atwood and Bennett (1979)	NA
$r_{FT} = \frac{k P_{CO} P_{H_2}}{P_{CO} + a P_{H_2O}}$	Fe/Cu/K	265	0.062	NA	0.58	Kuo (1984)	NA
$r_{FT} = \frac{k P_{CO} P_{H_2}}{P_{CO} + a P_{H_2O}}$	Precipitated Fe	270	0.018	NA	4.51	Nettelhoff et al. (1985)	NA
$r_{FT} = \frac{k P_{CO} P_{H_2}^2}{P_{CO} P_{H_2} + b P_{H_2O}}$	C-73 fused iron (United Catalysts Inc.)	232 248 263	0.013 0.025 0.042	NA	2.56 1.15 0.67	Huff and Satterfield (1984)	NA
$r_{FT} = \frac{k P_{CO} P_{H_2}}{P_{CO} + c P_{CO_2}}$	S6-10 fused iron (BASF)	240	0.010	NA	0.19	Nettelhoff et al. (1985)	NA
$r_{FT} = \frac{k P_{CO} P_{H_2}}{P_{CO} + c P_{CO_2}}$	Precipitated 100 Fe/1.3 K	220 240 250 260	0.0088 0.025 0.049 0.058	NA	0.255 0.210 0.229 0.237	Leadakowicz et al. (1985)	NA
$r_{FT} = k P_{H_2}$	Fused Fe/K	225-265	NA	147-265	NA	Dry et al.(1972)	1.2-7.2
$r_{FT} = \frac{k P_{CO} P_{H_2}}{(P_{CO} + K P_{H_2O})}$	Precipitated Fe/K/Cu	250	NA	220-441	NA	Zimmerman et al. (1990)	0.6-1.0

NA – Not Available

2.4.1 Alkyl mechanism

The mechanism was originally proposed by Fischer et al. (1926) and Crawford et al. (1939). Chain initiation takes place via dissociative CO chemisorption and formation of surface carbon. This surface carbon further hydrogenates, giving CH, CH₂ and CH₃ surface species. The CH₃ surface species is the chain initiator and the CH₂ surface species is a monomer. Chain growth takes place by subsequent addition of CH₂.

Initiation:

Monomer and chain initiator are formed as shown below:

Propagation:

The chain initiator and the monomer react by:

In subsequent propagation steps, the monomer is added as follows:

In general, the alkyl $\text{M-CH}_2\text{-CH}_2\text{R}$ is called the propagation-step intermediate product because it is formed in the propagation step and consumed by the termination step.

Termination:

The polymerization ends when the metal M is returned to its original state from the propagation-step intermediate product in one of three ways, leading to three primary products as shown below:

Primary products α -olefin and n-paraffins are formed by reactions (2.7) and (2.8) respectively. Note that the alkyl mechanism does not include the formation of branched hydrocarbons. Also, the alkyl mechanism cannot explain the formation of oxygenates in the FT synthesis (Schulz et al., 1988, 1990).

2.4.2 Alkenyl mechanism

Maitlis et al. (1996) proposed an alternate reaction pathway to predict the formation of olefins in FT synthesis.

Initiation:

The monomer is formed similar to Equation (2.10) by:

Now the chain initiator is formed by addition of the hydrogenated surface carbon to the monomer.

Propagation:

Chain propagation involves the addition of the methylene monomer to the chain initiator to form a surface allyl species. This is followed by an allyl-vinyl isomerization forming a surface alkenyl species:

In subsequent propagation steps, the monomer is added to the surface alkenyl to give a higher alkenyl species:

Termination:

Product desorption involves the hydrogen addition to the alkenyl species giving a α -olefin.

Note that this mechanism fails to explain the formation of n-paraffin as a primary product.

2.4.3 Enol Mechanism

Storch et al. (1951) proposed an alternate reaction scheme involving oxygen-containing surface species (enols). Two alternate monomers are postulated.

Initiation:

The chain initiator, or the main monomer and the alternate monomer are formed by addition of hydrogen to the carbon monoxide surface species.

In subsequent steps, the monomer M-CH₃ is added to the carbon monoxide surface species as follows:

Similarly, M=C (H)-OH can be formed by surface hydrogen:

Propagation:

Chain growth occurs between two enol species with elimination of water. The presence of an enol is due to the involvement of a C (R)-OH surface species.

Termination:

The termination process yields oxygenates and α-olefins as primary products. According to this mechanism, n-paraffins are formed secondarily by hydrogenation of α-olefins.

Oxygenate

Oxygenate

Oxygenate α -olefin n-paraffin

2.4.4 CO insertion mechanism

The CO insertion mechanism was originally proposed by Sternberg et al. (1959) and Roginski (1965). The CO insertion mechanism is viewed by many researchers as the main reaction leading to the formation of oxygenates (Anderson et al., 1985).

Initiation:

Chemisorbed CO is the monomer. The chain initiator, a surface methyl species, is formed through an alcohol intermediate by the addition of the monomer to hydrogen and removal of water:

Monomer Alcohol intermediate Chain initiator

Propagation:

The propagation step starts with the addition of the chain initiator $M-CH_3$ to the chemisorbed CO monomer forming a ketone intermediate surface species, $M-C(CH_3)=O$. This intermediate hydrogenates to an alcohol intermediate surface species, $M-CH(OH)-CH_3$. After removal of water and hydrogenation, the alcohol intermediate surface species yields the chain-growth intermediate surface species, $M-CH_2-CH_3$. The propagation step continues as:

Termination:

The chain-growth intermediate surface species $M-CH_2-R$ and the alcohol intermediate surface species $M-CH(OH)-R$ form n-paraffins and n-alcohols respectively on hydrogenation. Along with these products, the two intermediate surface species dehydrogenate to form α -olefins and aldehydes respectively.

2.5 IRON-BASED CATALYST COMPARED TO COBALT-BASED CATALYST

Iron and cobalt catalysts are both used industrially in Fischer-Tropsch synthesis (Pichler et al., 1952). The following features of comparison are used:

- a) Methanation
 - b) Chain growth
 - c) Chain branching
 - d) Water-gas shift reaction
 - e) Costs and catalyst availability
 - f) Response to temperature
 - g) Effect of partial pressure of CO
- a) Methanation

Methane formation has to be suppressed in FT-synthesis in favor of the formation of higher hydrocarbons. The iron catalyst is stable against excessive methane formation, even at high temperature (350°C) and low CO partial pressures (Riedel et al., 2003; Steynberg et al., 1999; Schulz et al., 1977).

The cobalt catalyst is strongly dependent on partial pressures of CO and H_2 and temperatures (Schulz et al., 1991; Schulz et al., 1971; Schulz et al., 1977). Methane formation is restricted at low

temperatures (180-220°C). Hence, cobalt is suitable for the low-temperature FT process (Schulz et al., 1977).

b) Chain growth

Chain growth increases with increasing partial pressure of carbon monoxide over cobalt catalysts. However, over iron catalysts, chain growth decreases with increasing partial pressure of carbon monoxide (Schulz et al., 2003).

c) Chain branching

For iron catalysts, branching becomes more favorable with time (Schulz et al., 2003). For cobalt catalysts, branching is more dominant at initial times but decreases with time (Schulz et al., 2001). Figure 2.1 (Schulz et al., 2003) shows the branching probability as a function of time and carbon number N_c (of the species to be branched) in FT synthesis with an iron catalyst. Figure 2.2 (Schulz et al., 2001) shows the branching probability as a function of time and carbon number N_c (of the species to be branched) in FT synthesis with cobalt catalyst. From Figures 2.1 and 2.2, it is clear that there is an opposite trend of probability of branching with time for iron and cobalt.

d) Water-gas-shift reaction

The water-gas-shift reaction is fast and easy to be seen on iron catalysts, but is difficult to be seen with cobalt catalyst (Teng et al., 2005).

When synthesis gas with a H_2/CO ratio of 2:1 can be obtained (for example, by autothermal reforming of methane), water-gas-shift activity will not be useful. Thus a cobalt-based catalyst can be suitable (Ma et al., 2006).

Figure 2.1 Branching probability as a function of carbon number N_c (of the species to be branched) and time in FT synthesis with iron catalyst (Schulz et al., 2003)

Figure 2.2 Branching probability as a function of carbon number N_c (of the species to be branched) and time in FT synthesis with cobalt catalyst (Schulz et al., 2001)

e) Costs of the catalyst

Only the metals Fe, Ni, Co and Ru have the required FT activity for commercial application. It has been shown that FT cobalt-based catalyst is effective. However the cost of cobalt-compared to iron-based catalyst is very high (Dry, 2002).

f) Response to temperature

The reaction temperature controls the chain length of the product molecules (Schulz et al., 2001). With an iron-based catalyst, the effect of increasing temperature is to reduce the chain length of the product molecules (Riedel et al., 2003). With a cobalt-based catalyst, the effect of increasing temperature is to reduce the average molecular size of the product. Also in addition to that, methanation and secondary olefin reactions of hydrogenation and isomerization are enhanced (Schulz et al., 1977; Schulz, 2003).

g) Effect of partial pressure of CO and H₂

With the iron catalyst, CO partial pressure and H₂ partial pressure have no strong influence on product distribution (Schulz, 2003; Schulz et al., 1994). With the cobalt catalyst, the CO partial pressure and H₂ partial pressure have strong influences on product distribution (Schulz et al., 1991; Schulz et al., 1971; Schulz et al., 1977).

2.6 STUDY OF IRON BASED CATALYST ACTIVITY

2.6.1 Preparation of the base catalyst

The incipient-wetness impregnation technique is used to prepare the catalyst supported on activated carbon. Other methods for catalyst preparation are the co-precipitation method and the sol-gel method. The incipient-wetness impregnation method involves mostly surface metal impregnation. But in case of co-precipitation and sol-gel, metal impregnation occurs throughout the pores of support (Liu et al., 2007). Also, the catalyst prepared by incipient-wetness impregnation loses its activity earlier compared to that of other methods (Liu et al., 2007).

2.6.2 Promotional effect of mixed metals on iron catalyst and selection of metals

Structural promoters are often added into the iron-based catalyst for the purpose of stabilizing catalyst crystals from sintering and to provide the catalyst with structural stability (Zhao et al., 2001;

Brien et al., 2001; Bukur et al., 2002). But catalysts containing structural promoters usually suffer from lower FTS activity due to strong metal-support interaction (Bukur et al., 1990; Wielers et al., 1989; Yang et al., 2005; Motjope et al., 2002). Therefore, to improve the performance of iron-based catalysts without sacrificing their activities and selectivities, chemical promoters, such as K, Cu, Mo etc., are often added into iron-based catalyst (Yang et al., 2004; Zhang et al., 2006; Ma et al., 2006). Cu and K promoters have been proved to improve the adsorption and dissociation of CO and play an important role in the FTS performances. Therefore, a large number of studies were carried out to investigate the relationship between K or Cu promoter and FTS performances of iron-based catalyst (Yang et al., 2004; Lohitharn et al., 2008; Wan et al., 2008; Ma et al., 2006).

2.6.2.1 Selection of copper (Cu) and potassium (K) as a promoter

As mentioned earlier, Cu and K promoters have been shown to promote both the reduction of iron as well as the adsorption and dissociation of CO (Yang et al., 2004; Li et al., 2002).

Cu and K addition studies by Wan et al. (2008) give H₂/CO usage ratios in FT synthesis. The H₂/CO usage ratio is the highest for the Fe/Cu catalyst and that of Fe/Cu/K catalyst is the lowest.

Similar work for the promotional effects of Cu and K on the behavior of Fe-based catalyst was carried out by Li et al. (2001) with varying K (K/Fe = 0, 0.02, 0.04) and Cu (Cu/Fe = 0, 0.01, 0.02) contents at 493 K and 464 psig.

From Table 2.2, addition of Cu to Fe-based catalyst increases CO conversion from 0.7 to 0.87 mol-CO/h /g-at.Fe. Addition of K similarly increases CO conversion from 0.7 to 1.23 mol-CO/h / g-at. Fe. Also, it is important to note that the addition of K alone decreases the methane selectivity from 4.8 to 1.8 % and increases the C₅₊ selectivity from 81.9 to 87.5%. On the other side, the addition of Cu alone increases methane selectivity from 4.8 to 10.2 %, and decreases the C₅₊ selectivity from 81.9 to 62.1%. But when both K and Cu are present, the tendency of Cu to produce methane nearly vanishes. When Cu/Fe = 0.02 and K/Fe = 0.02, methane selectivity decreases from 4.8 to 2% and the C₅₊ selectivity increases from 81.9 to 86.7%, similar to the results of K/Fe = 0.02 with no Cu, but with a higher conversion and hydrocarbon formation rates than the catalyst with K and no Cu .

Thus addition of Cu and K promoter improves the FTS activity and WGS reaction activity. As compared with the addition of Cu and K individually, the addition of both Cu and K keeps the excellent

stability and significantly improves the FTS and WGS activities. Due to weaker CO adsorption and stronger H₂ adsorption than the catalyst without Cu, chain growth is controlled. However, the addition of K promoter significantly improves the adsorption of CO and thus promotes the chain growth reaction.

Table 2.2 Steady-state performance of Fe₂O₃–Zn catalysts (Zn/Fe = 0.1) with different loadings of K and Cu (H₂/CO = 2, 493K, 464 psig, CO conversion 14–18%) (Li et al., 2001)

K/ Fe atomic ratio (× 100)	0	0	2	2	2	4
Cu/ Fe atomic ratio (× 100)	0	1	0	1	2	1
CO conversion rate (mol-CO/h /g at.-Fe)	0.70	0.87	1.23	2.4	2.43	2.49
CO ₂ formation rate (mol-CO/h /g at.-Fe)	0.02	0.06	0.10	0.30	0.32	0.30
Hydrocarbon formation rate (mol-CO/h /g at.-Fe)	0.68	0.81	1.13	2.10	2.11	2.19
CO ₂ selectivity (%)	2.3	6.5	8.5	12.3	12.9	12.1
CH ₄ selectivity (%)	4.8	10.2	1.8	1.8	2.0	2.5
C ₅₊ selectivity (%)	81.9	62.1	87.5	87.6	86.7	85.2

2.6.2.2 Selection of Molybdenum (Mo) as a promoter

Molybdenum has been reported to be moderately active for FTS, but very selective to light hydrocarbons (Schultz et al., 1967). The extent of WGS is high for Mo-based catalysts but decreases with time on stream (Ma et al., 2006). Schultz et al. (1967) first investigated the catalytic performance of molybdenum. They found that molybdenum has moderate activity in CO hydrogenation.

Ma et al. (2006) carried out a TPR study of Mo-promoted Fe-Cu-K/AC catalysts. The TCD signal response is shown in Figure 2.3. The first peak A is assigned to the reduction of Fe₂O₃ to Fe₃O₄. Peak B could be identified as due to the subsequent reduction of Fe₃O₄ to FeO. Peak C may be assigned to the reduction of FeO to metallic Fe. Peak D might be assigned to the reduction of a Mo-Fe oxide species formed at high temperatures during TPR. Peak A and B are much larger for 0% Mo than for 6% Mo and 12% Mo, suggesting that Mo addition significantly inhibits iron reduction. This suggests that a strong interaction exists between Mo and Fe oxides.

Figure 2.3 TPR profiles of different Mo-promoted Fe-Cu-K/AC catalysts (Ma et al., 2006)

Ma et al. (2007a) also studied the effect of Mo loading on CO conversion for iron-based catalyst. Figure 2.4 shows the important effects of Mo addition. The Mo-based catalyst shows a very slow deactivation rate compared to the Mo-free catalyst, indicating that Mo promoter improves the catalyst stability for longer times. A loading of 12% Mo decrease the active sites available for the reaction. Thus 6% Mo is considered to be optimum loading for iron-based catalyst supported on activated carbon (Ma et al., 2007a).

Figure 2.4 Effect of Mo loading on CO conversion (593K, 300 psig, 3 NL/gcat/h, $H_2/CO = 0.9$) (Ma et al., 2007a)

Ma et al. (2006) also studied the effect of Mo addition on product selectivities. From Table 2.3, the addition of Mo yields more methane and a smaller yield of C₅₊ hydrocarbons. This is probably due to Mo oxide in the catalyst weakening the C-O bond, resulting in a higher concentration of active carbon species on the surface of the Mo-promoted catalyst (Kip et al., 1987).

Table 2.3 Productivity and selectivity of hydrocarbon and Olefin-to-Paraffin ratio over different Mo-loaded Fe-Cu-K supported on activated carbon catalysts (593K, 3 NI/g-cat/h, 300 psig, H₂/CO = 0.9). All catalysts contain 15.7 wt % Fe, 0.8 wt % Cu, and 0.9 wt % K (Ma et al., 2006)

% Mo	0	6	12
Temperature (K)	593	593	593
TOS (h)	25-72	73-144	72-143
Productivity (g-HC/ g-cat/ h)	426-330	495-480	310-290
CH ₄ selectivity (%)	7.2	15	14.1
C ₂ -C ₄ selectivity (%)	39.6	45.6	40.6
C ₅₊ selectivity (%)	51.6	39.4	45.3
C ₂ -C ₄ Olefin/ Paraffin ratio	6.0	2.2	2.0

2.6.3 Effect of catalyst supports

We need to reduce the size of long-chain hydrocarbons formed in the FT synthesis. Activated carbon (AC) has been found to be a promising catalyst support for restricting hydrocarbon chain length. Some studies with AC-supported iron, cobalt and molybdenum-nickel catalysts indicate that chain length can be limited below C₃₅ over the AC support (Jung et al., 1982; Ma et al., 2005; Kugler et al., 2000). Table 2.4 shows the BET measurement results of different activated carbons. From Table 2.4, peat- and pecan-based activated carbons have smaller micropores compared to wood- and walnut-based AC. This means that peat- and pecan-based AC have greater fraction of mesopore volume.

Table 2.4 BET measurement result of activated carbon supports (Ma et al., 2007a)

AC type	Total Surface area (m ² /g)	Total Pore volume (cm ³ /g)	Fraction of pore volume present in the micropores
Peat	606	0.48	0.46
Wood	970	0.58	0.76
Pecan	1016	0.72	0.50
Walnut	892	0.52	0.64

From Figure 2.5, catalysts supported on peat- and pecan-based AC show high and steady CO conversion, compared to walnut- and wood-type activated carbons. This can be related to the large fraction of mesopore volume present in peat and pecan. Therefore, we need an AC such that it has a higher fraction of mesoporous volume.

Figure 2.5 Effect of carbon support type on CO conversion (593K, 300 psig, 3 NL/g-cat/h, $H_2/CO = 0.9$) (Ma et al., 2007a)

2.7 ZEOLITE STUDIES IN FISCHER TROPSCH PROCESS

2.7.1 Overview

Zeolites are microporous aluminosilicate minerals commonly used as commercial adsorbents. Zeolites are widely used in industry for water purification (Ellis et al., 1993), as heterogeneous catalysts for petrochemical hydrocracking and hydroisomerization (Usui et al., 2004), and in nuclear reprocessing. Their biggest use is in the production of laundry detergents. They are also used in medicine and in agriculture (Burriesci et al., 1984).

The zeolite chemical formula is $Na_nAl_nSi_{96-n}O_{192} \cdot 16H_2O$ ($0 < n < 27$). Zeolites are composed of several pentasil units linked together by oxygen bridges to form pentasil chains. A pentasil unit consists of eight five-membered rings (Garcia et al., 2010). In these rings, the vertices are Al or Si and an O atom is assumed to be bonded between the vertices. ZSM-5 has a high silicon-to-aluminum ratio, generally

30-80 molar ratios (Wiley et al., 1988). The microporous molecular structure of ZSM-5 molecules causes changes in their structure and reactivity (William et al., 1999; Rigby et al., 1997).

Shirazi et al. (2008) studied zeolites with different Si/Al ratios and compared the different properties of ZSM-5. BET specific surface areas of the synthesized zeolites increase with increasing Si/Al molar ratio. The particle size of the zeolite also increases with the increase in Si/Al ratio. Finally, Si/Al ratios affect the acidity of the samples and the total acid sites of ZSM-5 decrease with an increase in the Si/Al ratio.

The production of liquid fuels by the FT process suffers from two main constraints. One is that the polymerization-type kinetics of the FT reaction results in production of waxy compounds. The second is that the linear structure of the FT hydrocarbons (mostly n-paraffins) results in a fuel of too low quality to be directly blended into the gasoline and diesel pools due to low octane numbers and poor cold flow properties (Martinez et al., 2007). This is because linear aliphatic-chain liquid products (n-paraffins), which predominate in FT products, have lower research octane numbers (RONs) than i-paraffins (Huo et al., 2010). (The RON is determined by running the fuel in a test engine with a variable compression ratio under controlled conditions, and comparing the results with those from mixtures of i-octane and n-heptane, Nikolaou et al., 2004).

2.7.2 Effects of zeolite types on Fischer-Tropsch liquid distribution

The use of different zeolites (mordenite, erionite, ZSM-11, ZSM-12, L, Ω and β) in combination with an iron-based FT catalyst was studied by Hammer et al. (1994). Martinez et al. (2007) studied USY-500 (CBV500), USY-720 (CBV720), H-Beta (CP811), H-MOR (CBV20A), and HZSM-5 (CBV3020) zeolite types on the cracking of Fischer Tropsch wax.

The isomerization activity of zeolite in FT synthesis can be calculated from proton NMR spectra of the liquid synthetic product. The lower the value of the group ratio CH_2/CH_3 , the higher is the isomer content (Vytanova et al., 2006). Vytanova et al., (2006) also studied the effect of adding different zeolites on iron-based catalyst. The results are shown in Table 2.5.

From Table 2.5, it is clear that ZSM-5 zeolites have higher isomerization activity compared to other zeolites. Also, in terms of isomerizing activity under FT conditions, the test zeolites are arranged

in the order: ZSM-5 (80) > ZSM-5 (50) > ZSM-12 (90) > ZSM-5 (30) > β -75 > β -25 > Mn-Si > Al_2O_3 > Ce-Si > β -Si, where the numbers in parentheses refer to the Si/Al ratio.

Table 2.5 Isomerization activity zeolites added to Fe catalyst (Vytnova et al., 2006)

Zeolite types	CH_2/CH_3
None (Base Fe catalyst)	4.61
Al_2O_3	3.41
ZSM-5, Si/Al = 30	1.92
ZSM-5, Si/Al = 50	1.67
ZSM-5, Si/Al = 80	1.58
ZSM-12	1.82
β -75	2.20
β -25	2.33
Ce-Si	3.55
Mn-Si	3.03

Another important feature of zeolites is their cracking ability. Zeolites can decrease the long-chain waxy hydrocarbons to more useful liquid hydrocarbon such as gasoline and diesel (Zhao et al., 2010). Martinez et al. (2007) studied the activation and deactivation of zeolite with Co/SiO_2 catalyst. The FT liquid distribution over Co/SiO_2 -Zeolite catalyst is given in Table 2.6. From Table 2.6, for the ZSM-5 case, high yields of C_5 - C_{12} are obtained. Hence, ZSM-5 has a good cracking ability.

Table 2.6 Average hydrocarbon distribution (%C) for the base + zeolite hybrid catalysts (Martinez et al., 2007)

Hydrocarbon fraction	Base	Base + USY-500	Base + USY-720	Base + HBeta	Base + HMOR	Base + ZSM-5
C_1	11.8	12.0	11.6	11.5	11.0	11.0
C_2 - C_4	10.8	12.2	13.3	13.7	14.2	14.7
C_5 - C_{12}	41.0	44.4	48.6	57.3	55.8	62.2
C_{13} - C_{22}	28.3	24.9	21.3	16.4	16.8	11.0
C_{23+}	8.1	6.4	5.2	1.1	2.2	1.1

Further, methane formation at high temperatures is decreased when zeolite is added to iron-based FT catalyst (Schulz, 1999; Dry et al., 1981). The shape-selective properties of ZSM-5 limit the formation of hydrocarbons boiling above the gasoline range. The highly acidic nature of ZSM-5 gives

high activity for oligomerization, cracking, isomerization and aromatization. Finally, ZSM-5 has a medium pore size which makes this zeolite highly resistant to coking and stable under high temperature conditions (Botes et al., 2004).

CHAPTER 3

EXPERIMENTAL SETUP AND PROCEDURE

3.1 CATALYST PREPARATION PROCEDURE

3.1.1 Base catalyst preparation procedure

The method of catalyst preparation affects the catalyst activity. The following method is described by Ma et al. (2006) and is used in this work.

Activated carbon Norit SX Ultra (Sigma Aldrich) was used as a catalyst support. The activated carbon was stirred and washed twice in hot distilled water at 90°C for 2 hours. If Mo was required in the catalyst, then an amount of aqueous ammonium molybdate solution corresponding to 6% Mo was impregnated on the activated carbon support. The material was then dried in air at 90-100°C overnight. An aqueous solution containing ferric nitrate and cupric nitrate, corresponding to final iron and copper contents on the catalyst of 16 wt% and 0.8 wt %, respectively, was impregnated on the prepared Mo-activated carbon sample, again followed by drying in air 90-100°C overnight. An aqueous solution of potassium nitrate corresponding to 0.9 wt % K was the last to be put onto the sample, again followed by drying in air 90-100°C overnight. The detailed calculations of catalyst preparation are shown in Appendix E.

3.1.2 ZSM-5 catalyst

ZSM-5 (CBV 5524-G), was obtained from Zeolyst International. 10 Tons of pressure is applied in the hydraulically operated pelletizer to make ZSM-5 pellets. These pellets are ground on the 40 mesh size sieve and the 20-40 mesh ZSM-5 is then prepared using 20 and 40 mesh sieves. 20-40 mesh ZSM-5 is used throughout the experiments.

3.2 EQUIPMENT DESCRIPTION

The experimental setup consists of a reactor assembly, mass flow controllers, gas cylinders, chromatography setups, a computer interface controller and a chiller in a chemical hood. Gaseous compounds are analyzed by an online gas chromatograph (GC). Liquid is collected and analyzed by an offline GC.

The catalyst testing unit is shown in Figure 3.1 and is very similar to that used by Ma et al. (2006). The entire system is computer controlled using software InTouch by Wonderware. Most of the operating conditions (furnace temperature, gas flow rates etc.) can be directly set by the computer, except for the reactor pressure. The reactor pressure is manually controlled by the back-pressure regulator (BPR). An auto-injection gas sampler is available for the GC and is controlled from the computer.

The unit has three feeds: hydrogen, helium and syngas. The composition of syngas is 45% CO, 45% H₂, 5% He and 5% Ar. Helium and argon gases in the syngas mixture are used as internal standards. Each inlet line has one inlet isolation ball valve (B1) with a pressure gauge (P). The pressure gauges, in the range of 0-3000 psig, are obtained from Omega Engineering Inc. To protect lines from over-pressurization, each inlet line is connected to an independent pressure safety valve, also not shown in Figure 3.1. The outlets of the pressure safety valves are connected to the common vent manifold, not shown in Figure 3.1. Each feed gas line is further connected to a mass-flow controller (M.F.C.) followed by a regulator (R). The mass flow controllers are controlled by a common computer-interface controller. Each mass-flow controller has an operating range of 0-200 cc/min. The mass-flow controllers are model No. 5850 E, manufactured by Brooks Instruments. The regulator downstream of each mass flow controller helps in adjusting the outlet pressure as indicated by the pressure gauge installed downstream of the regulators. The regulator is followed by a check valve (not shown in Figure 3.1) and a second isolation ball valve (B2). A check valve ensures one-way flow of all the gases and avoids back mixing. The isolation ball valve B2 can be used for isolating one of the gas streams. Downstream of the regulator, each line is connected to a common reactor inlet manifold (shown by M in Figure 3.1) and then to the reactor inlet three-way bypass valve (TV1). The pressure of the reactor is indicated by a Sensotec pressure transmitter (model # THE/ 743-01) with an operating range of 0-2000 psig, not shown in Figure 3.1.

Figure 3.1 Equipment setup for Fischer Tropsch process

The reactor consists of a stainless-steel tube (SS 304L) of outer diameter of 0.5 in, tube length of 25 in, and wall thickness 0.049 in. Reactor tubes are made by TW Metals. The reactor is heated by a single-zone furnace supplied by Applied Test Systems. An ungrounded K-type thermocouple, (model KQSS-116-18), 1/16" diameter and 18" length with a 304 SS sheath, is used to monitor the catalyst bed temperature. The reactor contains the catalyst mixture in the centre, with the 1/16" quartz chips placed upstream and downstream in the catalyst bed. See below for details.

The exit gas stream from the reactor is passed through a back-pressure regulator from GO Inc (model P/N 101182) with an operating range 0-2000 psig. Liquids are condensed by a VWR chiller (Model #117-612) with an operating range from -20°C to 40°C and a capacity of 5.4 l/min. Water is used as the coolant. Liquids condensed are removed by a drain valve (shown in Figure 3.1) and analyzed later in the offline Varian GC.

Gases are analyzed in two types of detectors in the PerkinElmer GC. One is a thermal conductivity detector (TCD), which analyzes for the compounds H₂, CO, He, Ar, N₂, CH₄ and CO₂. The other is a flame ionization detector (FID), which analyzes hydrocarbons below carbon range C₆. Liquids are analyzed separately in an offline Varian GC by a flame ionization detector (FID), which analyzes the C₅₊ higher alkanes and alcohols.

3.3 EXPERIMENTAL PROCEDURE

Initially catalyst and quartz chips are loaded in the reactor. The reactor is pressure tested to avoid any leakages from fittings. Afterwards, the catalyst is pretreated with hydrogen. After the pretreatment, the reaction is started (Ma et al., 2006). See below for details.

3.3.1 Reactor loading

The stainless-steel reactor tube is cleaned and dried prior to each loading. Freshly prepared 20-40 mesh ZSM-5 is used for each reaction. 0.5 g of base catalyst is used in all the runs and three different weights of ZSM-5 (0.25, 0.5, and 1 g) are used. Two different bed arrangements are used. One is a separate-bed arrangement, in which the base catalyst is followed by the ZSM-5 catalyst. The catalysts are separated by quartz wool. For the case of the separate bed, the reactants pass through the base catalyst first, then through the ZSM-5. The other type of bed arrangement is the mixed bed, in which the base catalyst is intimately mixed with ZSM-5. In each type of bed arrangement, both the catalysts (base catalyst and ZSM-5 catalyst) are diluted 1:4 with 1/32" quartz chips. A thermocouple is carefully inserted in the middle of the catalyst bed. Above and below the catalyst bed and quartz wool, the reactor

is loaded with 1/16" quartz chips. Fresh quartz chips are used for every run. A Quartz wool plug is placed at the bottom of the reactor and it is then mounted in the furnace enclosure.

The system is then checked for possible leaks by flowing helium at 320 psig and room temperature. Then the reactor system fittings are checked with Snoop solution for any possible leaks. If there is any leak found, the reactor system is depressurized, the fitting is tightened and the test is repeated. The leak check is repeated until no leaks are detected.

In order to check for blank reactor activity, the reactor is loaded as stated above, except that there is no catalyst placed with the 1/32" quartz chips.

3.3.2 Pretreatment and reaction

After the reactor is tested for leaks, the catalyst is pretreated. During pretreatment, 200 cc/min of hydrogen is used at atmospheric pressure, and the reactor temperature is maintained at 400°C for 12 h. The GC is switched on only after ensuring that the carrier gases nitrogen and helium are flowing in the GC.

After the pretreatment, the reaction is started by setting the flows of the feed gases and the required temperature (as mentioned later in the Section 6.2.4) in the computer. The reaction pressure is set manually by means of the back-pressure regulator. The reactor outlet stream is passed through the chiller. The chiller temperature is maintained constant at 9°C. The chiller collects the compounds (higher alkanes, alcohols, etc.) above C₅₊ in the form of liquids, to be analyzed separately by the offline GC and auto sampler. The alkanes and olefins below carbon range C₆ are detected by the FID. Normally, the auto-injection sampling time for gas analysis is 15 min. The outlet gases from the GC are safely vented in the hood.

The liquid is collected in a 25-ml vial. The collected liquid has two phases, one is organic (oil) and other is aqueous. 3 h of settling time is given for all the liquid samples. The oil phase, being less dense compared to the aqueous phase, settles on top and the aqueous phase at bottom. The oil phase is carefully removed with an Eppendorf-type pipette, and the weight of both the samples (oil and aqueous phases) is measured. Finally, samples are prepared (as described in Appendix D) in a 2-ml vial, which is placed in the autosampler. The analysis time for the oil sample is fixed as 48 min, and for the aqueous sample as 28 min. Only the 24 – 48 h period liquid samples are used for the analysis. The validity of this

is confirmed by the stability tests to be discussed in Chapter 7. Chromatograph operating conditions for gas and liquid products are given in Appendix A. Gas and liquid calculations are shown in Appendix D.

Experimental results are shown in Chapters 5-7.

3.4 CHARACTERIZATION EQUIPMENT

3.4.1 Scanning Electron Microscopy and Energy-Dispersive X-Ray Spectroscopy

Scanning Electron Microscopy (SEM) gives information about the surface morphology of a sample, while Energy-Dispersive X-Ray Spectroscopy (EDX) gives information about the elemental composition. The surface morphology of the catalysts was determined by a Hitachi S-4700 scanning electron microscope at an accelerated voltage of 10 kV. The samples were prepared on a double-stick adhesive carbon tape mounted on specimen stubs and then sent into the SEM chamber. The SEM is equipped with an energy-dispersive spectrometer. Results before reaction are shown in Chapter 4, and results after reaction are shown in Chapter 8.

3.4.2 X-Ray Diffraction

X-Ray Diffraction (XRD) uses X-rays to find the crystalline structure, chemical composition, and physical properties of materials. X-ray diffraction measurements of the base catalyst before the reaction are carried out using PANalytical X'Pert Pro X-ray Diffractometer with Cu K α radiation (1.54184Å) at room temperature. It is equipped with an X'Celerator Detector System, Theta-Theta goniometer and 45-position sample changer. A software-controlled data acquisition system (X'Pert High Score and X'Pert Quantify) is used for peak ID and profile searches. About 0.5 g of sample with spacer is taken on the sample holder and placed in the sample stager.

3.4.3 Temperature-Programmed Reduction

Temperature-Programmed Reduction (TPR) is used to find the degree of reduction of the catalyst. A U-tube is filled with catalyst, and the air is removed using flowing inert gas. Hydrogen is added by mass flow controllers and a temperature program is initiated. The exit gas is analyzed by TCD detector. When reduction takes place, hydrogen is consumed by the reaction and the change in hydrogen content of the exit stream is picked up by the detector. Using the amount of hydrogen consumed, the degree of reduction (DOR) can be calculated as:

$$\text{DOR} = \frac{\text{Actual experimental H}_2\text{consumed}}{\text{Theoretical H}_2\text{consumed}} \times 100 \quad \dots (3.1)$$

Total amount of H₂ consumed between 200-800°C is considered for turn over number calculations. Reactions from (3.2) to (3.4) are occurring on the base catalyst as the temperature is increased in TPR. After stoichiometric balance, Equation (3.5) is used for the calculation of theoretical H₂ consumption. Theoretical H₂ consumption calculations for the base catalyst TPR are shown in Section 4.3.

3.4.4 Brunauer, Emmett and Teller surface area

Brunauer, Emmett and Teller (B.E.T.) surface area is measured with a Micrometrics Accelerated Surface Area and Porosimetry System (ASAP) 2020 to determine the total surface area. A sample of about 0.2 g is taken in previously weighted sample tube and the total weight is recorded. The sample tube is evacuated to about 100 milliTor and then backfilled with nitrogen twice using the Micrometrics VacPrep 06. After the second backfill, it is degassed under vacuum at 300°C for 1 h and cooled down to room temperature. The weight of the dried sample weight is recorded. The cooled sample tube is then connected to the ASAP 2020. The ASAP 2021 uses liquid nitrogen to do the absorption tests, and the analysis takes about 16 h.

3.5 SAFETY REQUIREMENTS

The process is operated at pressures as high as 400 psig and temperatures as high as 400°C. Toxic chemical substances such as catalyst, acetone (for cleaning glass wares), liquid hydrocarbons and poisonous carbon monoxide gas are used. For this purpose, personal safety equipment is available. This includes face shields, dust masks, thermal gloves (for handling of high-temperature vessels), safety goggles, an apron, and latex gloves are always worn while handling chemicals or working with equipment. Eye washers are available in the laboratory, to be used in the event of chemical spill in the eyes. Also there are fire extinguishers available in the laboratory, to be used in the event of fire.

Equipment shutdown switches are available inside the laboratory in case of fire or emergency. Along with the safety equipment, there are safety signs, warnings signs available inside the laboratory to ensure safe work all the time.

The reaction mixture produces hydrocarbon gases, including methane which is highly flammable. The unused hydrogen and carbon monoxide gases in the outlet stream are also flammable. The chemical hood is operated with the exhaust fan on, and this ensures safe discharge of these gases. The hood doors are normally kept closed. There are hood alarms for CO and H₂S. The alarms are monitored by the computer. The unit is shut automatically by the computer in the event of hood failure, fire, power failure, CO detection or H₂S detection, or if the flow of any reaction gas or the reaction temperature exceeds the corresponding set value.

The Material Safety Data Sheet file is maintained in the laboratory for all chemicals. A Material Safety Data Sheet (MSDS) contains basic information intended for safety with a material. The MSDS is very useful in the event of chemical poisoning etc., by providing guidelines for antidotes, etc.

CHAPTER 4

CATALYST CHARACTERIZATION BEFORE REACTION

4.1 SCANNING ELECTRON MICROSCOPY (SEM) AND ENERGY-DISPERSIVE X-RAY SPECTROSCOPY (EDX) ANALYSIS

Figure 4.1 is a low-magnification micrograph of the surface of the base catalyst before reaction. The lighter areas are richer in metals such as iron, molybdenum, copper, and potassium, while the darker areas are richer in carbon. The area in the white rectangle is further magnified and shown in Figure 4.2. The white rectangles in Figure 4.2 show the metals impregnated on the support.

Figure 4.1 SEM low magnification image of surface of the base catalyst before reaction

Figure 4.2 Magnified SEM image of surface of the base catalyst before reaction

EDX analysis was carried out to confirm the metals impregnated on support and to find the composition. Figure 4.3 shows the EDX of a portion of the catalyst particle shown by the white rectangle in Figure 4.1. EDX confirms the presence of iron, molybdenum, copper, and potassium metals on support. Notice that the concentrations of copper and potassium are very low because the metal loading for these metals are 0.8 wt% and 0.9 wt% respectively on support. Also note that the concentration of iron is higher than molybdenum because the metal loading for iron is 16 wt% and for molybdenum is 6 wt%. The carbon peak is highest because of the activated carbon support.

Figure 4.4 shows the EDX of the fresh ZSM-5 sample. The presence of Au and Pd is due to the coating material used while in the analysis. EDX of fresh ZSM-5 shows silicon, aluminum, and oxygen. The concentration of Si is higher due to the high molar ratio of Si/Al ($= 50$) in ZSM-5. The oxygen present is in the form of hydrogen aluminum silicate hydrate, as explained in Section 4.2 and Figure 4.6.

Figure 4.3 EDX analysis of surface of the base catalyst before reaction

Figure 4.4 EDX elemental analysis of fresh ZSM-5

4.2 X-RAY DIFFRACTION ANALYSIS

Figure 4.5 shows the x-ray diffraction (XRD) analysis of fresh base catalyst. The base catalyst is reduced before the XRD under H_2 flow of 200 sccm, at 400°C for 2 h. The base catalyst shows mainly graphite and Fe_3O_4 (magnetite phase). The graphite phase is due to the activated carbon, and the magnetite phase is due to reduction of $\alpha\text{-Fe}_2\text{O}_3$ to Fe_3O_4 .

Figure 4.5 XRD of fresh base catalyst

Figure 4.6 shows XRD of fresh ZSM-5. It shows the presence of hydrogen aluminum silicate hydrate phase. This is also reported by Shan et al. (1999).

Figure 4.6 XRD of fresh ZSM-5

4.3 TEMPERATURE-PROGRAMMED REDUCTION

Figure 4.7 shows TPR profiles of the base catalyst, 2:1 and 1:1 ratios of the base catalyst to ZSM-5, and fresh ZSM-5. For all the TPR profiles (except ZSM-5), the peak between 200-300°C is the reduction of α -Fe₂O₃ to Fe₃O₄. Also, in this region, CuO is reduced to Cu metal. Due to the low concentration of Cu in the base catalyst compared to Fe, this peak is not seen. From 350-500°C, Fe₃O₄ is reduced to FeO. In the range of 550-750°C, there is a broad peak that shows that FeO is reduced to Fe metal.

Figure 4.7 TPR profiles (a) 50 mg of base catalyst, (b) 33.33 mg of base catalyst and 16.67 mg of ZSM-5 (2:1), (c) 25 mg of base catalyst and 25 mg of ZSM-5 (1:1), (d) 50 mg of ZSM-5

The hydrogen consumption in Figure 4.7 (a) is greater than those in (b) and (c). The higher hydrogen consumption is due to the higher amount of the base catalyst. Table 4.1 shows the weights measured and hydrogen consumed amounts during TPR. Catalyst # 1 in Table 4.1 shows TPR results from a catalyst identical to the base catalyst but containing no Fe. This catalyst was prepared by Welshans (2011) and the area under that curve corresponds to adsorption on the support and all constituents except Fe and ZSM-5. The amount of experimental hydrogen consumption corresponding to the catalyst # 1 is subtracted in the calculation of degree of reduction (DOR) for all the catalysts. Note that hydrogen consumption for ZSM-5 is zero. Theoretical H₂ consumed is calculated using Equation (3.5) and DOR is calculated using Equation (4.1). Theoretical H₂ consumed calculations for catalyst # 2 are shown below:

We know that 0.16 g of Fe is supported on 1 g of activated carbon, and similarly for other metals (0.8%Cu, 0.9% K, and 6%Mo).

$$\text{So the actual weight \% of Fe is } \Rightarrow \frac{0.16 \times 100}{1 + 0.16 + 0.008 + 0.009 + 0.06} = 12.9345 \%$$

We know, 56 g of Fe is equivalent to 1 mol of Fe

$$\text{Therefore, 12.9345\% Fe of 1 g of base catalyst is equivalent to } \Rightarrow \frac{0.129345 \times 1}{56} = 0.00231 \text{ mol} = 2310 \mu\text{mol of Fe.}$$

From Equation (3.5), 2 mol of Fe need 3 mol H₂

$$2310 \mu\text{mol of Fe-at. need } \Rightarrow 2310 \times 3/2 = 3465 \mu\text{mol of H}_2$$

Therefore, theoretical H₂ consumed on 1 g of base catalyst = 3465 μmol of H₂

The amounts of theoretical H₂ consumption, actual experimental hydrogen consumption and DOR corresponding to the catalysts in Table 4.1 are found by:

DOR =

$$\frac{\left\{ \left(\frac{\text{Experimental H}_2 \text{ consumed}}{\text{g of catalyst}} \right) - \left[\left(\frac{\text{Experimental H}_2 \text{ consumed for catalyst \#1 (0\% Fe)}}{\text{g of catalyst \# 1}} \right) \times \left(1 - \frac{\text{g of Fe}}{\text{g of base catalyst}} \right) \times \left(\frac{\text{g of base catalyst}}{\text{g of catalyst}} \right) \right] \right\} \times 100}{\left\{ \left(\frac{\text{Theoretical H}_2 \text{ consumed}}{\text{g of base catalyst}} \right) \times \left(\frac{\text{g of base catalyst}}{\text{g of catalyst}} \right) \right\}}$$

... (4.1)

Table 4.1 Degree of reduction calculations for different catalysts

Catalyst #	Catalyst	Weight (mg)	Experimental H ₂ consumed (μmol/g of catalyst)*	Theoretical H ₂ consumed (μmol/g of catalyst)	Actual experimental H ₂ consumed (μmol/g of catalyst)	DOR (%)
1	0%Fe, 6 %Mo, 0.8%Cu, 0.9%K on Norit Ultra SX	49.1	498	-	0	-
2 (Base catalyst)	16%Fe, 6 %Mo, 0.8%Cu, 0.9%K on Norit Ultra SX	48.6	1353	3465	909	26.5
3	Base catalyst / ZSM-5 (1:1)	49.0	620	1732.5	403	23.3
4	Base catalyst / ZSM-5 (2:1)	48.0	774	2310	485	21.0
5	Fresh ZSM-5 (no base catalyst)	49.4	0	-	-	-

*Total amount of H₂ consumed between 200-800°C as one peak based H₂ consumption by AgO reference material.

4.4 BRUNAUER, EMMETT AND TELLER (B.E.T.) SURFACE AREA

B.E.T. surface area measurement is done for Norit SX Ultra activated carbon and compared with the value found by Ma et al. (2007a).

$$\text{B.E.T. surface area} = 927 \text{ m}^2/\text{g}. \quad \dots (4.2)$$

$$\text{B.E.T. surface area} = 1016 \text{ m}^2/\text{g} \text{ (Ma et al., 2007a)}. \quad \dots (4.3)$$

It can be seen that B.E.T. surface area measured for Norit SX Ultra activated carbon is consistent with Ma et al. (2007a).

CHAPTER 5

FISCHER-TROPSCH REACTIONS CARRIED OUT WITHOUT BASE CATALYST

5.1 INTRODUCTION

FT reactions are carried out first without any catalyst, to see the activity of the blank reactor, then with the ZSM-5 catalyst, and with the activated carbon (AC) used as the support for the base catalyst. The operating conditions are: syngas flow=100 scc/min, temperature = 300°C, pressure = 300 psig, H₂/CO ratio = 1.0.

5.2 RESULT AND DISCUSSION

5.2.1 FISCHER-TROPSCH REACTIONS CARRIED OUT WITHOUT BASE CATALYST

Table 5.1 shows the reaction data for the reaction carried out without base catalyst. All the reactions show negligible activity towards conversion of CO and H₂. Moreover, there are no FID peaks detected and no liquid products are collected.

This very low conversion of CO and H₂ is due to minor activity of the SS reactor tube, which has Fe, at 300°C. CO and H₂ conversions reported in the following chapters and in Appendix F.1 are the actual conversions of the particular reaction minus the conversion corresponding to the blank reactor.

Table 5.1 Fischer-Tropsch data for the reactions without base catalyst (syngas flow=100 scc/min, Temperature = 300°C, Pressure = 300 psi, H₂/CO ratio = 1.0, TOS = 0 - 48 h)

Reaction details	Catalyst weight (g)	CO conversion (%)	H ₂ conversion (%)	Products in FID	Liquid product (g)
Blank reactor without any catalyst	0.00	0.16	2.80	No peak detection in FID	No liquid collected
Reactor with ZSM-5 only without base catalyst	0.50	0.25	1.60	No peak detection in FID	No liquid collected
Reactor with Norit SX Ultra AC	0.50	0.19	1.50	No peak detection in FID	No liquid collected

CHAPTER 6

FISCHER-TROPSCH REACTIONS CARRIED OUT WITH BASE AND ZSM-5 CATALYST

6.1 INTRODUCTION

Operating conditions for these runs (with the base catalyst, with and without ZSM-5) are as before: syngas flow=100 scc/min, temperature = 300°C, pressure = 300 psig, H₂/CO ratio = 1.0. The effect of ZSM-5 weight change on product selectivities in separate-bed catalyst arrangement and mixed-bed catalyst arrangement are analyzed. Products formed in both the arrangements are compared. The effect of temperature change on product selectivities in the separate-bed catalyst arrangement is analyzed.

6.2 RESULT AND DISCUSSION

6.2.1 EFFECT OF ZSM-5 WEIGHT CHANGE ON PRODUCT DISTRIBUTION IN SEPARATE-BED CATALYST ARRANGEMENT

The quantity of base catalyst is fixed at 0.5 g for all the reactions. Three different ZSM-5 amounts (0.25, 0.5, and 1 g) are used in the separate-bed catalyst arrangement. Gas, oil, and aqueous product analyses are carried out. The results are discussed below in detail.

6.2.1.1 Overall Products

The amounts of all hydrocarbons are shown in Table 6.1. The C₅-gases from the FID are included as C₅ i-paraffins because these gases are not detected as n-paraffins or as olefins. The detailed analysis of products is described in subsequent sections.

From Table 6.1, for the base catalyst alone, the amounts of C₁₋₄ are larger than total C₅₊. But the product profile shifts towards total C₅₊ when 0.25 g of ZSM-5 is added to the base catalyst. This is because ZSM-5 oligomerizes and aromatizes olefinic-gas components coming from the base catalyst, and also ZSM-5 converts alcohols formed by the base catalyst to hydrocarbons. More details on oligomerization of these gas molecules are shown in Section 6.2.1.3. Further addition of ZSM-5 causes cracking, and an increase in amounts of C₁₋₄ can be seen in Table 6.1. The total hydrocarbons (gas and liquid included) increase slightly with ZSM-5 and the amounts of alcohols are nearly zero. This means that the additional ZSM-5 is converting alcohols into hydrocarbons. This is consistent with Bjorgen et

al. (2007) and Calsavara et al. (2008). ZSM-5 amounts greater than 0.5 g basically convert all the alcohols to hydrocarbons and water.

Table 6.1 Overall product distribution (separate-bed catalyst arrangement, 0.5 g of base catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 psi, TOS = 24 – 48 h)

ZSM-5 weight (g)	0	0.25	0.5	1
Bed arrangement	Base catalyst	Separate-bed		
Compounds	g carbon/day			
C ₁	2.31	1.95	2.21	2.81
C ₂₋₄	6.12	5.41	6.05	6.95
Sum of C ₁₋₄ (Gas)	8.43	7.36	8.26	9.76
Total C ₅₊ (Gas + Liquid)	6.19	8.00	8.05	7.05
Sum of hydrocarbons (Gas + Liquid)	14.62	15.36	16.31	16.81
Total alcohols	0.75	0.01	0.00	0.00
CO ₂	14.39	15.56	15.10	15.50
Unreacted CO	6.84	5.27	4.30	5.12

6.2.1.2 WGS and FTS reaction activities

Figure 6.1 shows activities of WGS and FTS reactions in the base catalyst and in the separate-bed arrangement. The rates are calculated similar to the procedure followed by Ma et al. (2007b). The calculations are tabulated in Appendix F.2. From Figure 6.1, the rates of the two reactions seem approximately constant with ZSM-5 weight addition. Therefore ZSM-5 is inactive towards FTS and WGS reactions. Mahay et al. (1987) also confirm that ZSM-5 alone cannot show any activity towards WGS. EDX of a spent sample of ZSM-5 is shown in Figure 8.1. This confirms no migration of metals (Fe, Cu) from the separate bed to ZSM-5, as opposed to results from the mixed-bed configuration, shown later in Chapter 8.

Figure 6.1 WGS and FTS reaction rates (mmol/min). Separate-bed catalyst arrangement, 0.5 g of base catalyst, Si/Al ratio in ZSM-5 = 50, H_2/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 psi, TOS = 24 – 48 h.

6.2.1.3 Gas analysis

All the data in described in this Section are tabulated in Appendix F.3. Figure 6.2 shows that the amounts of CH_4 , C_3H_8 , $i-C_4H_{10}$, $n-C_4H_{10}$, $i-C_5H_{12}$, and $n-C_5H_{12}$ detected by the FID increase with ZSM-5. The additional amounts of ZSM-5 provide more cracking activity sites (Martinez et al., 2005).

From Figure 6.2, the amount of CH_4 generated by the separate bed with 0.25 g ZSM-5 is lower than that of the base catalyst. This is because ZSM-5 forms a C_1 carbenium ion (Fejes et al., 1984) and this ion further reacts with another carbenium-based molecule to form long-chain hydrocarbons. Larger amounts of ZSM-5 increase the cracking of longer-chain hydrocarbons (Martinez et al., 2005) to form increased amounts of n -paraffins C_3H_8 , etc. No $i-C_4H_{10}$ and $i-C_5H_{12}$ are found in the products with the base catalyst alone because the base catalyst lacks the acidic active sites responsible for isomerization, but these are available with ZSM-5. The amounts of $i-C_4H_{10}$ and $i-C_5H_{12}$ increase with ZSM-5 because ZSM-5 provides isomerization active sites (Borges et al., 2007).

Figure 6.2 Gas-phase paraffins detected by FID (g carbon/day). Separate-bed catalyst arrangement, 0.5 g of base catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 psi, TOS = 24 – 48 h.

Figure 6.3 shows the effect of ZSM-5 on olefins and other gases that are not shown in Figure 6.2. C₂H₆ and C₂H₄ are reported together here because both have similar retention times. The production of C₂H₆ + C₂H₄ is initially flat and then decreases with addition of more ZSM-5. The cracking of long-chain hydrocarbons by ZSM-5 may increase the amount of C₂H₆ (Martinez et al., 2005). This may be offset by the oligomerization of C₂H₄ by ZSM-5 (Knifton et al., 1994). C₂H₄ oligomerises because C₂H₄ is an unsaturated hydrocarbon and more reactive compared to C₂H₆. When relatively large amounts of ZSM-5 are present, oligomerization could be more significant.

From Figure 6.3, the base catalyst with no ZSM-5 produces greater amounts of C₃H₆, 1-C₄H₈, and t-C₄H₈ compared to that when ZSM-5 is added. This is because the base catalyst does not have the acidic sites responsible for oligomerization. On the other hand, the acidic sites of ZSM-5 convert C₃H₆, 1-C₄H₈, and t-C₄H₈ to other products (Knifton et al., 1994; Borges et al., 2007). Gases containing a double bond (C₃H₆, 1-C₄H₈ t-C₄H₈) are highly reactive and tend to oligomerize on the ZSM-5 active sites (Knifton et al., 1994; Borges et al., 2007).

Figure 6.3 FID gases not shown in Figure 6.2 (g carbon/day). Separate-bed catalyst arrangement, 0.5 g of base catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 psi, TOS = 24 – 48 h.

Also from Figure 6.3, the amounts of i-C₄H₈ and c-C₄H₈ increase for 0.25 g of ZSM-5 and decrease thereafter. These isomers are not formed with the base catalyst alone because it lacks the acidic active sites needed for isomerization (Borges et al., 2007). The decrease of these species with larger amounts of ZSM-5 can be explained by ZSM-5 causing them, double bonded and highly reactive, to undergo oligomerization. This is consistent with Knifton et al. (1994).

In Figure 6.3, C₅ gases are formed when the base catalyst alone is used, but the total amount decreases as ZSM-5 is increased. These C₅ gases are not n-alkanes or i-alkanes, and could be alkenes or i-alkenes. The decrease of the C₅-olefins could also be due to oligomerization into liquid products (Knifton et al., 1994).

6.2.1.4 Overall liquid production rates

Figure 6.4 shows overall liquid hydrocarbon production rates and overall alcohol production rates. The liquid hydrocarbon appears to go through a maximum around 0.5 g of ZSM-5. Larger amounts of ZSM-5 provide additional cracking active sites (Martinez et al., 2005) which decrease the

amount of liquids. This is consistent with the formation of additional gaseous C_1 to C_5 products, as seen in Figure 6.2.

Small amounts of ZSM-5 convert alcohols formed by the base catalyst to hydrocarbons (Bjorgen et al., 2007; Calsavara et al., 2008). Correspondingly, the production of alcohols decreases to nearly zero in the presence of even small amounts of ZSM-5, as can also be seen in Figure 6.4.

Figure 6.4 Liquid hydrocarbon and alcohol production rate (g/kg FT cat/h). Separate-bed catalyst arrangement, 0.5 g of base catalyst, Si/Al ratio in ZSM-5 = 50, H_2/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C , reactor pressure = 300 psi, TOS = 24 - 48 h.

6.2.1.5 Hydrocarbons distribution in organic liquid phase

All the amounts of liquids are shown in Appendix F.4. Figure 6.5 shows the amounts of n-paraffins in the organic liquid phase. The amounts of n- C_5 increase, and the amounts of n- C_8 to n- C_{22} decrease, with addition of ZSM-5. n- C_6 and n- C_7 go through a maximum at 0.25 g ZSM-5. ZSM-5 provides additional cracking sites (Martinez et al., 2005), and the long-chain paraffins n- C_8 to n- C_{22} are cracked into smaller-chain hydrocarbon molecules. The amount of n- C_5 increases with ZSM-5 and can be considered to be a small-chain cracked molecule. The increase in amounts of n- C_6 and n- C_7 for a

small amount of ZSM-5 might be due to rearrangements of small-chain gas molecules. These amounts further decrease because increased ZSM-5 provides cracking and aromatization active sites.

Figure 6.5 Liquid n-paraffins (g carbon/day). Separate-bed catalyst arrangement, 0.5 g of base catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 psi, TOS = 24 - 48 h.

Figure 6.6 shows the amounts of i-paraffins in the organic liquid phase. The amounts of i-C₅ and i-C₆ increase monotonically with increase in ZSM-5 weight. This is because additional ZSM-5 provides additional cracking active sites (Martinez et al., 2005). i-C₇ through i-C₁₂ pass through a maximum with ZSM-5 loading between 0.25 g and 0.5 g. Higher hydrocarbons are present in amounts too small to show significant changes. So the molecules i-C₇ to i-C₂₂ probably crack to small-chain molecules similar to i-C₅, and consistent with Figure 6.2. The amounts of C₂₃₊ are too low to show any significance.

Figure 6.6 Liquid i-paraffins (g carbon/day). Separate-bed catalyst arrangement, 0.5 g of base catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 psi, TOS = 24 - 48 h.

Aromatic ring compounds were not reported by Ma et al. (2006) because the base catalyst lacks acidic active sites for aromatization. However, ZSM-5 oligomerizes and aromatizes small-chain olefin molecules (Zang et al., 2010). The combination of the base catalyst and ZSM-5 produces aromatic products like toluene, p-xylene, propyl-benzene, and butyl-benzene as seen in Figure 6.7. It is important to note that all these aromatic compounds are alkyl-benzenes. This means that ZSM-5 is selective towards alkyl-benzene compounds. ZSM-5 is shape selective (Stocker, 2005) and it allows only certain molecules to flow in and out of the pores relatively easily. This is because steric hindrance of other molecules, such as m-xylene, o-xylene, and 2,3-methyl ethyl-benzene, is higher compared to alkyl benzene. Therefore it is difficult for sterically hindered molecules to desorb from ZSM-5 pores and the converse is also true.

From Figure 6.7, the amounts of toluene and p-xylene increase monotonically with ZSM-5. This is because ZSM-5 provides additional oligomerization active sites and hence a greater tendency towards aromatization (Degnan, 2000). Propyl-benzene and butyl-benzene appear to go through a maximum around 0.5 g ZSM-5. Additional ZSM-5 probably causes cracking of the propyl and butyl chains

attached to the benzene ring. Also from Figure 6.7, the amounts of butyl-benzene are lower than other aromatics. This can be explained by noting that butyl-benzene is bulky and has more steric hindrance. Thus butyl-benzene is difficult to desorb from ZSM-5 pores.

Production of high amounts of i-C₅ to i-C₁₂ and aromatics together gives hydrocarbons in the high-octane gasoline range using the separate bed with increasing amounts of ZSM-5. From Appendix F.4, the largest amount of aromatics and isomers for the separate bed is with the base catalyst and ZSM-5 in the ratio of 1.

Figure 6.7 Aromatic compounds (g carbon/day). Separate-bed catalyst arrangement, 0.5 g of base catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 psi, TOS = 24 - 48 h.

6.2.1.6 Alcohols and water in aqueous liquid phase

From Table 6.2, the base catalyst with no ZSM-5 shows the largest amounts of alcohols. Addition of ZSM-5 to the base catalyst shows an increased formation of water. This is because ZSM-5 has activity towards converting alcohols to hydrocarbons and water (Bjorgen et al., 2007; Calsavara et al., 2008). Thus all the alcohol amounts in Table 6.2 are nearly zero. It can also be seen that 0.25 g of

ZSM-5 is sufficient to convert nearly all the alcohols into hydrocarbons. The alcohols that are the most resistant to ZSM-5 are 2-propanol and 2-butanol, which can be expected to be bulkier.

Table 6.2 Aqueous-phase compounds (separate-bed catalyst arrangement, 0.5 g of base catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 psi, TOS = 24 – 48 h)

ZSM-5 weight (g)	0	0.25	0.5	1
Bed arrangement	Base catalyst	Separate-bed		
Compounds	Weights in aqueous phase (mg)			
Methanol	243	0	0	0
Ethanol	516	0	2	0
2-Propanol	92	103	5	3
1-Propanol	272	0	0	0
2-Butanol	31	14	0	5
1-Butanol	205	0	0	0
2-Pentanol	0	0	0	0
1-Pentanol	157	0	0	0
Sum of alcohols	1516	118	7	8
Water	894	2282	2295	2493

Overall reaction (FTS, WGS, cracking, oligomerization, isomerization, aromatization, conversion of alcohols to hydrocarbons, and coke formation) sequence in the separate bed is sketched and shown in Figure 6.8.

FTS: Fischer-Tropsch Synthesis by the base catalyst

Figure 6.8 Sketch of an overall reaction sequence

6.2.2 EFFECT OF ZSM-5 WEIGHT CHANGE ON PRODUCT DISTRIBUTION IN MIXED-BED CATALYST ARRANGEMENT

As in the separate-bed arrangement, three different ZSM-5 weights (0.25, 0.5, and 1 g) are used with 0.5 g base catalyst in the mixed-bed catalyst arrangement. Gas, oil, and aqueous product analyses are carried out. The results are discussed below in detail.

6.2.2.1 Overall Products

Conversion data are shown in Appendix F.1. Table 6.3 shows the amounts of all hydrocarbons. These numbers are compared to those in Table 6.1, corresponding to the separate-bed arrangement, in Section 6.2.3. In this section, we discuss the effect of increasing the amounts of ZSM-5 in the mixed-bed arrangement.

From Table 6.3, the amounts of C_{1-4} and total C_{5+} are higher for the base catalyst alone compared to the amounts of these species when ZSM-5 is added in the mixed-bed arrangement. The low activity of physical mixtures of the base catalyst and ZSM-5 is also reported by Botes et al. (2004). The decline in activity in the mixed bed is due to lowering of the alkali content of the iron catalyst due to alkali migration from FT catalyst to ZSM-5 (Botes et al., 2004). Incorporation of Cu and K promoters to an iron-based catalyst was found to have significant influences on the adsorption and reduction behaviors, as well as on catalytic performances during FTS (Wan et al., 2008). Hence the changes in H_2 adsorption and CO adsorption significantly affect the FTS performance of the mixed-bed catalyst arrangement. It was attempted to confirm the alkali migration from the FT catalyst to the ZSM-5 by EDX analysis of spent ZSM-5. EDX of a spent sample of ZSM-5, shown in Figure 8.2, confirms alkali migrations of metals. The product distribution of individual hydrocarbons is discussed in Section 6.2.2.3 and Section 6.2.2.5.

The total amount of alcohols over the base catalyst alone is higher than the total alcohols produced in the mixed-bed catalyst arrangement, and the amounts decrease with increasing amounts of ZSM-5. This means that additional ZSM-5 converts alcohols into hydrocarbons and water (Bjorgen et al., 2007; Calsavara et al., 2008).

From Table 6.3, the amount of CO_2 formed over the base catalyst is greater than the amounts of CO_2 formed when ZSM-5 is added. The amounts of unreacted CO for all the reactions with ZSM-5 are

higher than the base catalyst amounts and therefore ZSM-5 affects FTS activity in the mixed bed. As described before, the decline in FT activity in the mixed bed is due to lowering of the alkali content of the iron catalyst because of alkali migration from FT catalyst to ZSM-5 (Botes et al., 2004). The higher amounts of CO₂ are also ascribed to the higher CO conversion in the base catalyst compared to the mixed-bed catalyst arrangement.

Table 6.3 Overall product distribution (mixed-bed catalyst arrangement, 0.5 g of base catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 psi, TOS = 24 – 48 h)

ZSM-5 weight (g)	0	0.25	0.5	1
Bed arrangement	Base catalyst	Mixed-bed		
Compounds	g carbon/day			
C ₁	2.31	1.20	1.34	2.27
C ₂₋₄	6.12	3.81	3.85	4.87
Sum of C ₁₋₄ (Gas)	8.43	5.01	5.19	7.14
Total C ₅₊ (Gas + Liquid)	6.19	4.64	5.15	4.34
Sum of hydrocarbons (Gas + Liquid)	14.62	9.65	10.34	11.48
Total alcohols	0.75	0.35	0.22	0.10
CO ₂	14.39	9.85	10.34	13.96
Unreacted CO	6.84	15.83	14.98	8.58

6.2.2.2 WGS and FTS reaction activities

The activities of WGS and FTS reactions in the base catalyst and the mixed-bed arrangement are calculated similar to the procedure followed by Ma et al. (2007b). The calculations are tabulated in Appendix F.2. From Figure 6.9, the WGS and FTS rates decrease with the addition of a small amount of ZSM-5, and then increase with additional ZSM-5. The initial decrease in WGS and FTS rates for ZSM-5 is probably due to alkali migration from FT catalyst to ZSM-5 (Botes et al., 2004), as mentioned earlier. The further increase in these rates with ZSM-5 is not clearly understood, but these values are relatively lower than the base catalyst alone. So alkali migration definitely reduces the activity of the base catalyst in the mixed bed, as opposed to results from the separate-bed configuration.

Figure 6.9 WGS and FTS reaction rates (mmol/min). Mixed-bed catalyst arrangement, 0.5 g of base catalyst, Si/Al ratio in ZSM-5 = 50, H_2/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 psi, TOS = 24 - 48 h.

6.2.2.3 Gas analysis

All the data are shown in Appendix F.3. Figure 6.10 shows that the amounts of CH_4 , C_3H_8 , $i-C_4H_{10}$, $n-C_4H_{10}$, $i-C_5H_{12}$, and $n-C_5H_{12}$, as detected by the FID, increase with ZSM-5. As in the separate-bed case, the amount of CH_4 generated by the base catalyst alone is large compared to the mixed bed with 0.25 and 0.5 g ZSM-5. This is because ZSM-5 forms a C_1 carbenium ion (Fejes et al., 1984) and this ion further reacts with another molecule on ZSM-5 to form longer-chain hydrocarbons. Larger amounts of ZSM-5 increase the cracking of long-chain hydrocarbons (Martinez et al., 2005) and this increases the amount of methane formed. C_3H_8 , $n-C_4H_{10}$, and $n-C_5H_{12}$ do not increase appreciably with the addition of ZSM-5. Neither $i-C_4H_{10}$ nor $i-C_5H_{12}$ is found in the base catalyst alone because the base catalyst lacks the acidic active sites responsible for isomerization. The amounts of $i-C_4H_{10}$ and $i-C_5H_{12}$ increase with ZSM-5 because it provides isomerization sites (Borges et al., 2007).

Figure 6.10 Gas-phase paraffins detected by FID (g carbon/day). Mixed-bed catalyst arrangement, 0.5 g of base catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 psi, TOS = 24 – 48 h.

Figure 6.11 shows the effect of ZSM-5 on olefin and other gases that are not shown in Figure 6.10. As in Figure 6.3, C₂H₆ and C₂H₄ are reported together here because both have similar retention times. In contrast to Figure 6.3, the production of these gases drops rapidly with addition of 0.25 g ZSM-5 and then levels off. This is partly because of the cracking of long-chain i-paraffins to C₂H₆ (Martinez et al., 2005), as can be seen in later in Figure 6.14, and partly because of the oligomerization of C₂H₄ (Knifton et al., 1994). Increasing amounts of ZSM-5 provide more active sites for oligomerization (Knifton et al., 1994). Hence C₂H₄ oligomerizes because C₂H₄ is an unsaturated hydrocarbon and more reactive compared to C₂H₆.

From Figure 6.11, the base catalyst with no ZSM-5 produces greater amounts of C₃H₆, 1-C₄H₈, and t-C₄H₈ compared to the mixed-bed catalyst arrangement with ZSM-5. This is because the base catalyst does not have the acidic sites responsible for oligomerization. On the other hand, the acidic sites of ZSM-5 convert C₃H₆, 1-C₄H₈, and t-C₄H₈ to other products (Knifton et al., 1994; Borges et al., 2007). In the absence of ZSM-5, c-C₄H₈ is not produced. The double-bond-containing gases (C₃H₆, 1-C₄H₈ t-

C₄H₈) are highly reactive and tend to oligomerize on ZSM-5 active sites (Knifton et al., 1994; Borges et al., 2007).

Figure 6.11 FID gases not shown in Figure 6.10 (g carbon/day). Mixed-bed catalyst arrangement, 0.5 g of base catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 psi, TOS = 24 – 48 h.

As before, i-C₄H₈ is not formed with the base catalyst alone because the base catalyst lacks the acidic active sites needed for isomerization (Borges et al., 2007). As in the separate bed, the amount of i-C₄H₈ in the mixed bed increases for 0.25 g of ZSM-5 and decreases thereafter. As before, the decrease of i-C₄H₈ with larger amounts of ZSM-5 can be explained by saying that further addition of ZSM-5 causes i-C₄H₈, double bonded and highly reactive, to undergo oligomerization (Knifton et al., 1994).

As in Figure 6.3, C₅ gases (alkenes or i-alkenes) are formed when the base catalyst alone is used but decrease as ZSM-5 is increased. The decrease of the C₅-olefins is also due to oligomerization into liquid products (Knifton et al., 1994).

6.2.2.4 Overall liquid production rates

Figure 6.12 shows overall liquid hydrocarbon and overall alcohol production rates for the base catalyst and the mixed bed. The hydrocarbon production rate drops with ZSM-5 change from 0 to 1 g.

Also, the production of alcohols decreases for change in ZSM-5 from 0 to 1 g. The decrease in hydrocarbon production is due to alkali migration from the FT catalyst to ZSM-5 and also due to the additional cracking sites available on ZSM-5. Also, ZSM-5 has activity towards converting some of the alcohols formed by the base catalyst to hydrocarbons (Bjorgen et al., 2007; Calsavara et al., 2008).

Figure 6.12 Liquid hydrocarbon and alcohol production rate (g/kg FT cat/h). Mixed-bed catalyst arrangement, 0.5 g of base catalyst, Si/Al ratio in ZSM-5 = 50, H_2/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 psi, TOS = 24 – 48 h.

6.2.2.5 Hydrocarbon distribution in organic liquid phase

Figure 6.13 shows the amounts of individual n-paraffins in the organic liquid phase. The amounts of n-C₅ to n-C₂₂ paraffins are much higher for the base catalyst compared to the mixed bed with 0.25 g ZSM-5. This is because the base catalyst follows polymerization kinetics giving high amounts of long-chain hydrocarbons, and the addition of ZSM-5 to the base catalyst causes cracking of these hydrocarbons. The amount of n-C₅ increases and the amounts of n-C₆ to n-C₂₂ decrease, with increase in ZSM-5 from 0.25 to 1 g. This is because additional ZSM-5 provides additional active sites to crack long-chain paraffins n-C₆ to n-C₂₂ to smaller-chain molecules like n-C₅.

Figure 6.13 Liquid n-paraffins (g carbon/day). Mixed-bed catalyst arrangement, 0.5 g of base catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 psi, TOS = 24 - 48 h.

Figure 6.14 shows the amounts of individual i-paraffins in the organic liquid phase. The amounts of i-C₅ to i-C₁₂ paraffins are much lower for the base catalyst compared to the mixed bed with 0.25 g ZSM-5. This is because the base catalyst does not have isomerization sites. The addition of ZSM-5 to the base catalyst causes isomerization of n-paraffins forming large amounts of gasoline-range isomers. On the other hand, the amounts of i-C₁₃₊ are higher for the base catalyst compared to the mixed bed with 0.25 g ZSM-5. This is because addition of ZSM-5 to the base catalyst causes cracking of long-chain i-C₁₃₊ molecules.

From Figure 6.14, with the addition of 0.5 g ZSM-5 to the base catalyst, the amounts of i-C₅ and i-C₉ decrease, while i-C₆ to i-C₈ and i-C₁₀₋₂₂ increase slightly. This is because the addition of 0.5 g ZSM-5 to the base catalyst causes isomerization of n-paraffins (Borges et al., 2007). Further addition of ZSM-5 leads to cracking of i-C₆ to i-C₂₂ compounds. Higher hydrocarbons (C₂₃₊) are present in amounts too small to show significant changes.

Figure 6.14 Liquid i-paraffins (g carbon/day). Mixed-bed catalyst arrangement, 0.5 g of base catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 psi, TOS = 24 - 48 h.

As mentioned earlier, aromatic ring compounds were not reported by Ma et al. (2006) because the base catalyst lacks acidic active sites for aromatization. However, ZSM-5 oligomerizes and aromatizes small-chain olefin molecules (Zang et al., 2010). The combination of the base catalyst and ZSM-5 shows aromatic products like toluene, p-xylene, propyl-benzene, and butyl-benzene. Figure 6.15 shows the amounts of different aromatic hydrocarbons for the mixed-bed catalyst arrangement with different amounts of ZSM-5 added to the base catalyst. As in the separate-bed experiments, all these aromatic compounds are alkyl-benzenes.

From Figure 6.15, the amounts of all the aromatics increase when ZSM-5 increases from 0 to 0.5 g, similar to the behavior in the separate bed. This is because ZSM-5 provides additional oligomerization active sites and hence more tendency towards aromatization (Degnan, 2000). Unlike the separate-bed arrangement, further addition of ZSM-5 causes all these species to decrease. This is because additional ZSM-5 provides more cracking active sites, and alkyl chains attached to these aromatic compounds crack to give smaller aromatic species and small-chain paraffins. Again, ZSM-5 favors toluene, p-xylene and propyl-benzene more than butyl-benzene. This can be explained by noting

that butyl-benzene is bulky and has more steric hindrance. Therefore butyl-benzene is difficult to desorb from ZSM-5 pores.

As in the separate-bed case, production of high amounts of $i\text{-C}_5$ to $i\text{-C}_{12}$ and aromatics together gives high-octane gasoline-range hydrocarbons in the mixed bed with increasing amounts of ZSM-5. Comparing the amounts of $i\text{-C}_5$ to $i\text{-C}_{12}$ plus aromatics in the mixed bed, it is seen that the maximum amount is formed in the mixed bed with 0.5 g ZSM-5. However, this amount is less than that formed in the separate bed with 0.5 g ZSM-5.

Figure 6.15 Aromatic compounds (g carbon/day). Mixed-bed catalyst arrangement, 0.5 g of base catalyst, Si/Al ratio in ZSM-5 = 50, H_2/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C , reactor pressure = 300 psi, TOS = 24 – 48 h.

The overall reaction sequence in the mixed bed also follows the similar sequence to the separate bed. The overall reaction sequence is shown in Figure 6.8.

6.2.2.6 Alcohols and water in aqueous liquid phase

As for the separate bed, the base catalyst shows the highest amounts of alcohols compared to the mixed bed (Table 6.4). This is because ZSM-5 has activity towards converting alcohols to hydrocarbons (Bjorgen et al., 2007; Calsavara et al., 2008). Unlike the separate bed, even 1 g ZSM-5 is not sufficient

to convert most of the alcohols. The acidic sites of ZSM-5 are affected by alkali migration from the FT catalyst, similar to the discussion in Section 6.2.2.1. Also from Table 6.4, the water produced increases slightly, because ZSM-5 converts alcohols to hydrocarbons and water.

Table 6.4 Aqueous-phase compounds (mixed-bed catalyst arrangement, 0.5 g of base catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 psi, TOS = 24 - 48 h)

ZSM-5 weight (g)	0	0.25	0.5	1
Bed arrangement	Base catalyst	Mixed-bed		
Compounds	Weights in aqueous phase (mg)			
Methanol	243	126	128	64
Ethanol	516	247	273	94
2-Propanol	92	50	44	25
1-Propanol	272	118	102	30
2-Butanol	31	17	17	12
1-Butanol	205	94	93	14
2-Pentanol	0	0	0	0
1-Pentanol	157	77	32	0
Sum of alcohols	1516	728	687	239
Water	894	472	813	2061

6.2.3 QUANTITATIVE COMPARISONS BETWEEN SEPARATE BEDS AND MIXED BEDS

The distribution of individual products from the separate bed and the mixed bed has already been discussed in Section 6.2.1 and Section 6.2.2 respectively. The purpose of this section is to compare the separate bed and the mixed bed quantitatively, to find out whether there is any improvement in the product distribution if the bed arrangement is changed. To quantify the changes in amounts of gaseous hydrocarbons, liquid hydrocarbons, and aqueous products with changing reactor configuration, we define a delta value as;

$$\Delta X = (X \text{ in separate-bed catalyst arrangement}) - (X \text{ in the mixed-bed catalyst arrangement}) \quad \dots (6.1)$$

6.2.3.1 Delta values of overall products

Table 6.5 shows the delta amounts of overall products calculated using Equation (6.1). Overall product amounts in both the beds can also be found in Table 6.1 and Table 6.3. The delta values of C_1 , C_2 - C_4 , and total C_{5+} are positive for all the ZSM-5 amounts. This implies that higher amounts of these hydrocarbons are formed in the separate bed compared to the mixed bed. The positive values of Δ are due to the lowering of alkali content of the base catalyst following alkali migration to ZSM-5 in the mixed bed, as mentioned in the discussion of Section 6.2.2.1. There is no improvement in the total hydrocarbon production when the base catalyst and ZSM-5 are mixed.

Also from Table 6.5, the delta amounts of total alcohols are negative for all the ZSM-5 amounts. Lower amounts of alcohols are formed in the separate bed compared to the mixed bed. This is because, in the separate bed, all the alcohols formed by the base catalyst pass over all the ZSM-5 present and all the amounts are converted effectively to hydrocarbons and water. On the contrary, the mixed bed is unable to convert all the alcohols to hydrocarbons and water. This is probably because the acidic sites of ZSM-5 are affected by the alkali migration from FT catalyst, as discussed in Section 6.2.2.6. Hence, the conversion of alcohols to hydrocarbons and water is affected in the mixed bed.

From Table 6.5, the delta amounts of CO_2 are positive, and those of unreacted CO are negative, for all the ZSM-5 amounts. This means that higher amounts of CO_2 are formed, and higher amount of CO are converted, in the separate bed compared to the mixed bed. The higher amounts of CO_2 formed are due to higher CO conversion (partly due to FTS reaction and partly due to WGS reaction) in the separate-bed compared to the mixed bed, as shown in Appendix F.1. The lower conversion in the mixed bed is due to lowering of alkali content of the base catalyst due to alkali migration from FT catalyst to

ZSM-5, as discussed in Section 6.2.2.1. There is no improvement in the CO conversions when the base catalyst and ZSM-5 are mixed.

Table 6.5 Delta amounts of overall products (0.5 g of base catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 psi, TOS = 24 – 48 h)

ZSM-5 weight (g)	0.25	0.5	1
Compounds	Δ (Compound) g carbon/day		
C ₁	0.75	0.87	0.54
C ₂₋₄	1.6	2.2	2.08
Sum of C ₁₋₄ (Gas)	2.35	3.07	2.62
Total C ₅₊ (Gas + Liquid)	3.36	2.9	2.71
Sum of hydrocarbons (Gas + Liquid)	5.71	5.97	5.33
Total alcohols	-0.34	-0.22	-0.1
CO ₂	5.71	4.76	1.54
Unreacted CO	-10.56	-10.68	-3.46

6.2.3.2 Delta values of WGS and FTS reaction activities

Table 6.6 shows the delta rates of WGS and FTS calculated using Equation (6.1). The detailed data are shown in Appendix F.2. The delta rates of WGS and FTS are positive for all the ZSM-5 amounts. The activities of WGS and FTS are higher in the separate bed compared to the mixed bed. The lower amounts of WGS and FTS rates in the mixed bed are due to lowering of the alkali content of the base catalyst due to alkali migration from FT catalyst to ZSM-5, as discussed in Section 6.2.2.1. There is no alkali migration in the separate bed, as discussed in Section 8.1. Hence, there is no improvement in the WGS and FTS rates when the base catalyst and ZSM-5 are mixed.

Table 6.6 Delta amounts of WGS and FTS reaction rates (0.5 g of base catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 Psi, TOS = 24 - 48 h)

ZSM-5 weight (g)	0.25	0.5	1
Rates	Δ (Rate) mmol/min		
rWGS	0.33	0.27	0.09
rFTS	0.36	0.35	0.15

6.2.3.3 Delta amounts of gas products

Table 6.7 shows the delta amounts of CH₄, C₂H₆ + C₂H₄, C₃H₈, C₃H₆, i-C₄H₁₀, n-C₄H₁₀, 1-C₄H₈, i-C₄H₈, t-C₄H₈, c-C₄H₈, i-C₅H₁₂, n-C₅H₁₂, and C₅-gas hydrocarbons calculated using Equation (6.1). The detailed data for these gas hydrocarbons are shown in Appendix F.3.

Table 6.7 Delta amounts of gas products (0.5 g of base catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 Psi, TOS = 24 – 48 h)

ZSM-5 weight (g)	0.25	0.5	1
Products	Δ (Product) g carbon/day		
CH ₄	0.75	0.87	0.54
C ₂ H ₆ + C ₂ H ₄	0.88	0.89	0.58
C ₃ H ₈	0.32	0.99	1.22
C ₃ H ₆	-0.41	-0.50	-0.57
i-C ₄ H ₁₀	0.22	0.57	0.92
n-C ₄ H ₁₀	0.24	0.68	0.73
1-C ₄ H ₈	-0.16	-0.20	-0.14
i-C ₄ H ₈	0.59	-0.09	-0.41
t-C ₄ H ₈	-0.04	-0.06	-0.15
c-C ₄ H ₈	-0.04	-0.09	-0.09
i-C ₅ H ₁₂	0.14	0.41	0.42
n-C ₅ H ₁₂	0.17	0.15	0.19
C ₅ -gas	-0.02	-0.29	-0.30

From Table 6.7, the delta amounts of CH₄, C₂H₆ + C₂H₄, C₃H₈, i-C₄H₁₀, n-C₄H₁₀, i-C₄H₈, i-C₅H₁₂, and n-C₅H₁₂ are positive. The higher amount of these hydrocarbons in the separate bed is due to

cracking and isomerization reactions over the ZSM-5. These reactions occur to a lower extent in the mixed bed. The negative delta values for C₃H₆, 1-C₄H₈, t-C₄H₈, c-C₄H₈, and C₅-gas (higher amounts in the mixed bed) are due to the decrease of oligomerization active site on ZSM-5 in that configuration. The decrease in these active sites in the mixed bed is due to alkali migration from the base catalyst to the ZSM-5, as discussed in Section 8.1.

6.2.3.4 Delta amounts of overall liquid production rates

Table 6.8 shows the delta amounts of overall hydrocarbon and overall alcohol production rates calculated using Equation (6.1). The detailed amounts of these production rates are shown in Figure 6.4 and Figure 6.11.

From Table 6.8, the delta amounts of hydrocarbon production are positive for all the ZSM-5 amounts. The activities of WGS and FTS are higher in the separate bed compared to the mixed bed, as discussed in Section 6.2.3.2. Higher WGS and FTS rates give higher hydrocarbon production rates. On the other hand, the delta amounts of alcohol production are negative in the mixed bed. The mixed bed is unable to convert all the alcohols to hydrocarbons and water. This is probably because the acidic sites of ZSM-5 are affected by the alkali migration from FT catalyst, as discussed in Section 6.2.3.1. Hence, there is no improvement in hydrocarbon production rate and the conversion of alcohols to hydrocarbons and water when the base catalyst and ZSM-5 are mixed.

Table 6.8 Delta amounts of hydrocarbon and alcohol production rates (0.5 g of base catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 Psi, TOS = 24 – 48 h)

ZSM-5 weight (g)	0.25	0.5	1
Production rates	Δ (Rate) g/Kg FT cat./h		
Hydrocarbon production	295.00	265.00	215.83
Alcohol production	-50.82	-56.79	-19.31

6.2.3.5 Delta amounts of hydrocarbons in organic liquid phase

Table 6.9 shows the delta amounts of liquid hydrocarbons calculated using Equation (6.1). The detailed data for these hydrocarbons are shown in Appendix F.4.

From Table 6.9, the delta amounts of liquid n-C₅ are positive for all ZSM-5 amounts. This implies that amounts of n-C₅ are higher in the separate bed, probably because the cracking of long-chain hydrocarbons is greater compared to mixed bed. The cracking activity of ZSM-5 is reduced in the mixed bed due to alkali migration from FT catalyst, as discussed in Section 6.2.3.1. For n-C₆ to n-C₁₄ the values are generally positive for ZSM-5 amounts 0.25 and 0.5 g, and these values are generally negative for higher amount of ZSM-5. The increase in these values in the separate bed for ZSM-5 amounts 0.25 and 0.5 g is probably because the cracking of long-chain hydrocarbons is greater in the separate bed than the mixed bed. The negative values of n-C₆ to n-C₁₄ species are also due to greater cracking effect in the separate bed, but the amounts of CH₄, C₂H₆ + C₂H₄, C₃H₈, i-C₄H₁₀, n-C₄H₁₀, i-C₅H₁₂, and n-C₅H₁₂ gases increase, as per the discussion of Table 6.7 in Section 6.2.3.3, at higher ZSM-5 amounts in the separate bed compared to the mixed bed. So at higher ZSM-5 amounts, n-C₆ to n-C₁₄ species are more cracked to smaller-chain species in the separate bed than the mixed bed. The overall effect is the cracking of long-chain hydrocarbons is greater in separate bed than the mixed bed for all ZSM-5 amounts. For n-C₁₅₊ the values are generally negative. This implies that the amounts of n-C₁₅₊ are higher in the mixed bed, probably because cracking activity of ZSM-5 is reduced in the mixed bed due to alkali migration from FT catalyst, as discussed in Section 6.2.3.1. Hence, there is no improvement in cracking of long-chain hydrocarbons when the base catalyst and ZSM-5 are mixed. The delta values of n-paraffins are relatively smaller than the delta values of i-paraffins and aromatics.

From Table 6.9, the delta amounts of liquid i-C₅ to C₁₅ are generally positive. For i-C₁₆₊ the values are generally negative. The amounts of i-C₅ to C₁₅ are generally higher in the separate bed and the amounts of i-C₁₆₊ are generally higher in the mixed bed. ZSM-5 is active towards the cracking of long-chain hydrocarbons and the isomerization of n-paraffins formed by the base catalyst, more so in the separate bed than the mixed bed. Cracking and isomerization activities of ZSM-5 are reduced in the mixed bed due to alkali migration from FT catalyst, as discussed in Section 6.2.3.1. Hence, there is no improvement in isomerized hydrocarbons when the base catalyst and ZSM-5 are mixed.

Table 6.9 Delta values of liquid paraffins and aromatic compounds in organic liquid phase (separate-bed and mixed-bed catalyst arrangement, 0.5 g of base catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 Psi, TOS = 24 - 48 h)

ZSM-5 weight (g)	0.25	0.5	1
n-paraffins	Δ (n-paraffin) mg carbon/day		
n-C ₅	60.9	59	66.3
n-C ₆	136.4	134.8	-42.3
n-C ₇	338	33.5	-80.1
n-C ₈	152	5.5	-39.1
n-C ₉	87.3	6.4	-24.7
n-C ₁₀	76.7	16.3	-15.2
n-C ₁₁	68.7	25.7	7.1
n-C ₁₂	11.5	3.9	-0.9
n-C ₁₃	3.1	-4.7	-2.9
n-C ₁₄	11.9	1.8	11.2
n-C ₁₅	-4.3	-7.1	2.8
n-C ₁₆	-7.5	-7.8	2.7
n-C ₁₇₊	-10.2	-21.8	1.6
i-paraffins	Δ (i-paraffin) mg carbon/day		
i-C ₅	148	-6.9	333.7
i-C ₆	52.3	50.8	95.2
i-C ₇	985.1	320	73.8
i-C ₈	606.7	299.1	-25
i-C ₉	176.7	238.2	126.1
i-C ₁₀	102	200.2	185.4
i-C ₁₁	21.3	79.9	62.7
i-C ₁₂	27.6	190.1	90.4
i-C ₁₃	8.5	90.4	83.3
i-C ₁₄	6.4	48.5	65.1
i-C ₁₅	4.5	12.2	30.5
i-C ₁₆	9.3	-0.7	18.7
i-C ₁₇₊	-1.9	-3.9	8.3
Aromatics	Δ (aromatic) mg carbon/day		
toluene	19.2	314.2	650.4
p-xylene	-20.2	379	554.8
propyl- benzene	-21.2	270.3	280.4
butyl-benzene	11.2	44.5	22.7

From Table 6.9, the delta amounts of liquid aromatics are generally negative for small amounts of ZSM-5, and positive for 0.5 and 1 g ZSM-5. The amounts of aromatics are higher in the separate bed. ZSM-5 is active towards aromatization and oligomerization of olefins formed by the base catalyst in the

separate bed. Aromatization and oligomerization activities of ZSM-5 are reduced in the mixed bed due to alkali migration from FT catalyst, as discussed in Section 6.2.3.1. Hence, there is no improvement in aromatic hydrocarbons when the base catalyst and ZSM-5 are mixed.

The overall reaction sequence in the both the beds are similar. The amounts of all the hydrocarbons in the mixed bed are generally lower than those of the separate bed. This is mainly due to the metal migration in the mixed bed, as mentioned earlier. Hence, the extent of hydrocarbon rearrangement reactions in the separate bed might be higher. The overall reaction sequence for the separate bed is already shown in Figure 6.8.

6.2.3.6 Delta values of alcohol products and water in the aqueous liquid phase

Table 6.10 shows the delta amounts of alcohol products and water in the aqueous liquid phase calculated using Equation (6.1). The detailed data for these aqueous liquid compounds are shown in Appendix F.4.

From Table 6.10, the delta amounts of all alcohol products and water are generally negative for all the ZSM-5 amounts used, except for 2-pentanol. Lower amounts of alcohols are formed in the separate bed compared to the mixed bed. This is because all the alcohols formed by the base catalyst in the separate bed pass over all the ZSM-5 present and all the amounts are converted effectively to hydrocarbons and water. Higher amounts of water are formed in the separate bed due to the higher conversion of alcohols to hydrocarbons. On the other hand, the mixed bed is unable to convert all the alcohols to hydrocarbons and water, probably because the acidic sites of ZSM-5 are affected by alkali migration from the FT catalyst, as discussed in Section 6.2.2.6. Hence, there is no improvement in the conversion of alcohols to hydrocarbons and water when the base catalyst and ZSM-5 are mixed.

Table 6.10 Delta amounts of alcohol products and water in the aqueous liquid phase (separate-bed and mixed-bed catalyst arrangement, 0.5 g of base catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 Psi, TOS = 24 - 48 h)

ZSM-5 weight (g)	0.25	0.5	1
Aqueous product	Δ (Product) mg carbon/day		
Methanol	-47.3	-47.8	-24.2
Ethanol	-129	-141.8	-49.2
2-Propanol	32.3	-23.8	-13.9
1-Propanol	-70.6	-61.2	-17.9
2-Butanol	-1.8	-10.7	-4.8
1-Butanol	-60.7	-60.3	-9
2-Pentanol	0.1	0	0
1-Pentanol	-52.4	-21.5	0
	Δ (Product) mg/day		
Water	1809.9	1294.5	45.4

6.2.4 EFFECT OF TEMPERATURE IN BASE CATALYST AND IN SEPARATE-BED CATALYST ARRANGEMENT

The effect of temperature is studied for the base catalyst alone and in the separate bed. The quantities of the base catalyst and the ZSM-5 are fixed in the reactor. Analyses of gas, oil, and aqueous product are carried out. The results are discussed below in detail, using the sketch of the overall reaction sequence in Figure 6.8 as a guide.

6.2.4.1 Overall Products

The detailed amounts of gas and liquid components are given in Appendix F.3 and Appendix F.4 respectively. Table 6.11 gives the overall amounts of reactor outlet compounds. The effect of temperature change on the overall product distribution is discussed here, and more details are provided in subsequent sections.

From Table 6.11, the amounts of C_{1-4} are higher than total C_{5+} at a given temperature for the base catalyst and the separate bed. Note that there is a significant decrease in amounts of total C_{5+} at 320°C for the separate bed. The decrease in these amounts in the base catalyst at 320°C is not much significant. This means that the rates of reactions involving C_5 as a reactant (cracking and isomerization) increase more than the rates of FT reactions forming C_5 . Therefore E_{act} for cracking and isomerization reactions are higher than E_{act} for forming C_5 (Smit et al., 2008; Bizreh et al., 1984; Wei, 1996). Similarly, there is a sharp increase in total hydrocarbons between 280-300°C (especially for the separate bed), then a smaller rise (for the base catalyst) or a small decrease (for the separate bed) between 300-320°C. The sharp rise in total hydrocarbons in the separate bed between 280-300°C is mainly because of conversion of alcohols to hydrocarbons by ZSM-5, and because of oligomerization of small-chain hydrocarbons (formed by the base catalyst) to liquid hydrocarbons on ZSM-5. More details on the increase in the hydrocarbon rate are given in Section 6.2.4.4. The smaller decrease in total hydrocarbons for the separate bed between 300-320°C is inconsistent with the smaller rise for the base catalyst, probably due to the small variations in the amount of unreacted CO.

Alcohols increase with increase in temperature using the base catalyst, but no net alcohols are produced in the separate bed at higher temperatures. So E_{act} for hydrocarbon to alcohol is greater than E_{act} for hydrocarbon formation (Felmer et al., 1981).

From Table 6.11, the respective amounts of CO₂ and unreacted CO at a given temperature are nearly the same for both the base catalyst and the separate bed. As expected, ZSM-5 does not participate in the conversion of CO or in the formation of CO₂. Only the base catalyst is active towards conversion of CO and in formation of CO₂. The amounts of CO₂ are low at lowest temperature, and these level off to nearly constant higher values at higher temperatures for both the base catalyst and the separate bed. Also, it can be seen that the amounts of unreacted CO are high at lowest temperature, and these level off to nearly constant low values at higher temperatures for both the base catalyst and the separate bed. The decrease in CO and increase in CO₂ amounts with increasing temperatures are because high temperature favors FTS and WGS reactions to occur on the base catalyst.

Table 6.11 Effect of temperature on products from the base catalyst and the separate-bed catalyst arrangement (0.5 g of base catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor pressure = 300 psi, TOS = 24 – 48 h)

Temperature (°C)	280		300		320	
Bed arrangement	Base catalyst	Separate-bed	Base catalyst	Separate-bed	Base catalyst	Separate-bed
ZSM-5 weight (g)	0	0.5	0	0.5	0	0.5
Compounds	g carbon/day					
C ₁	0.72	0.89	2.31	2.21	3.23	3.79
C ₂₋₄	2.77	2.25	6.14	6.05	7.43	7.07
Sum of C ₁₋₄ (Gas)	3.49	3.14	8.45	8.26	10.66	10.86
Total C ₅₊ (Gas + Liquid)	2.68	2.57	6.19	8.05	5.05	4.41
Sum of hydrocarbons (Gas + Liquid)	6.17	5.71	14.62	16.31	15.71	15.26
Total alcohols	0.25	0.03	0.75	0	1.06	0
CO ₂	10.2	8.81	14.39	15.1	14.2	15.12
Unreacted CO	18.5	18.51	6.84	4.3	4.2	5.17

6.2.4.2 WGS and FTS reaction rates

From Table 6.12, the respective rates of WGS and FTS at a given temperature are generally the same for both the base catalyst and the separate bed. Only the base catalyst is active towards conversion of CO (by FTS) and in the formation of CO₂ (by WGS). The addition of ZSM-5 has a negligible contribution in FTS and WGS rates with increase in temperatures. The rates of FTS and WGS are low at lowest temperature, and these levels off to generally higher constant values at higher temperatures for

both the base catalyst and the separate bed. Between 280-300°C, the FTS rates increase much more than the WGS rates.

Table 6.12 Effect of temperatures on reaction rates from the base catalyst and separate-bed catalyst arrangement (0.5 g of base catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor pressure = 300 psi, TOS = 24 - 48 h)

Temperature (°C)	280		300		320	
Bed arrangement	Base catalyst	Separate-bed	Base catalyst	Separate-bed	Base catalyst	Separate-bed
ZSM-5 weight (g)	0	0.5	0	0.5	0	0.5
Rates	m mol/min					
rWGS	0.59	0.51	0.83	0.87	0.82	0.88
rFTS	0.26	0.36	0.89	0.99	0.88	0.77

6.2.4.3 Gas analysis

Table 6.13 shows the production of all the FID gases with increase in temperature for both the base catalyst and the separate bed. It can be seen that the amount of each hydrocarbon increases when the temperature is increased from 280 to 320°C.

From Table 6.13, the amounts of CH₄, C₃H₈, n-C₄H₁₀, and n-C₅H₁₂ increase with the temperatures in both the base catalyst and the separate bed. The amounts of CH₄ increase more than the amounts of C₃H₈ with increase in the temperature, and so on with n-C₄H₁₀, and n-C₅H₁₂. Hence the activation energy for the formation of species with low carbon number (like CH₄) could be higher than that for species with higher carbon number (like C₃H₈). Further, there might be cracking reactions occurring on long-chain hydrocarbons over the zeolite, and these could further change the product distribution for the separate bed.

From Table 6.13, the amounts of C₂H₆ + C₂H₄ increase in the base catalyst at higher temperatures, probably due to higher FTS rates. For the separate bed, the increases of C₂H₆ + C₂H₄ amounts are lower than those of CH₄, probably because the activation energy of methane formation is larger (92 KJ/mol vs. 84 KJ/mol [Felmer et al., 1981]). Further, there is increased oligomerization of C₂H₄ over ZSM-5 in the separate bed.

Table 6.13 Effect of temperature on gas-phase paraffins from the base catalyst and the separate-bed (0.5 g of base catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor pressure = 300 psi, TOS = 24-48 h)

Temperature (°C)	280		300		320	
Bed arrangement	Base catalyst	Separate-bed	Base catalyst	Separate-bed	Base catalyst	Separate-bed
ZSM-5 weight (g)	0	0.5	0	0.5	0	0.5
Compounds	g carbon/day					
CH ₄	0.72	0.89	2.31	2.21	3.23	3.79
C ₂ H ₆ + C ₂ H ₄	0.65	0.45	1.76	1.67	2.21	1.92
C ₃ H ₈	0.21	0.46	0.50	1.49	0.56	1.61
C ₃ H ₆	0.64	0.10	2.14	0.11	2.64	0.21
i-C ₄ H ₁₀	0.00	0.29	0.03	1.03	0.03	1.12
n-C ₄ H ₁₀	0.18	0.32	0.36	1.04	0.37	1.11
1-C ₄ H ₈	0.90	0.06	1.11	0.01	1.37	0.14
i-C ₄ H ₈	0.00	0.44	0.00	0.58	0.00	0.77
t-C ₄ H ₈	0.19	0.08	0.24	0.10	0.25	0.12
c-C ₄ H ₈	0.00	0.05	0.00	0.02	0.00	0.07
Sum of C ₂₋₄	2.77	2.25	6.14	6.05	7.43	7.07
i-C ₅ H ₁₂	0.00	0.27	0.03	0.78	0.04	0.81
n-C ₅ H ₁₂	0.21	0.27	0.33	0.41	0.30	0.43
C ₅ -gas	0.91	0.51	1.20	0.56	1.25	0.83
Sum of C ₅	1.12	1.05	1.56	1.75	1.59	2.07

From Table 6.13, the amounts of i-C₄H₁₀, and i-C₄H₈ are nearly zero for the base catalyst, and increase for the separate bed for all the temperatures. For the base catalyst, these species are not formed in appreciable amounts, compared to CH₄, C₃H₈, and n-C₄H₁₀, as mentioned earlier. For the separate bed isomerization reactions on ZSM-5 of these species are expected to increase with increasing temperatures. It is also important to note that the amount of i-C₄H₁₀ increases more than i-C₄H₈ or i-C₅H₁₂ with increasing temperatures. This means that the activation energy for i-C₄H₁₀ isomerization is larger than those of the other two species (Bizerh et al., 1984).

From Table 6.13, the amounts of C₃H₆, 1-C₄H₈, and t-C₄H₈ increase in the base catalyst at higher temperatures. For the separate bed, these amounts are lower than those of in the base catalyst, probably because the higher temperatures favor the oligomerization reactions over ZSM-5. This means that the

activation energies for oligomerization reactions could be larger than those formations of these species (Bizerh et al., 1984).

6.2.4.4 Overall liquid production rates

Table 6.14 shows the overall liquid production rates of hydrocarbons and the alcohols. For the base catalyst and the separate bed, there is an increase in the liquid hydrocarbon production rate when the temperature is increased from 280 to 300°C, but then drops with a further increase in temperature to 320°C. For the base catalyst, the increase in the hydrocarbon production rates is because high temperature favors the FTS reaction for production of gasoline-range liquid hydrocarbons, as seen in Section 6.2.4.5. Wei (1996) showed that activation energies of formation for long-chain hydrocarbon species decrease with increase in carbon number ($n=8-14$). Hence, a further increase in temperature (to 320°C) could favor C_{2-4} formation reactions (by FTS) which have higher activation energies compared to the formation of long-range liquid hydrocarbons. This is consistent with Table 6.13.

For the separate bed, from 280 to 300°C, overall liquid production rates of hydrocarbons increase to a much greater extent than for the base catalyst. Production in the separate bed then drops with a further increase in temperature to 320°C, also to a much greater extent than for the base catalyst. The increase in the hydrocarbon production rates could be because of an increase in one or more of the following reactions;

- a) The FTS reaction for production of liquid hydrocarbons due to the base catalyst.
- b) WGS reaction which produces hydrogen necessary for liquid hydrocarbon forming reactions on the base catalyst.
- c) Conversion of alcohols formed by the base catalyst to hydrocarbon and water on ZSM-5.
- d) Oligomerization of small-chain (less than C_5) hydrocarbon reactions occurring on ZSM-5.
- e) Aromatization and oligomerization of small-chain hydrocarbons together to form aromatic compounds containing reactions occurring on ZSM-5.

The further increase in temperature to 320°C could decrease the production rate of liquid hydrocarbons because of increased cracking of long-chain hydrocarbons, and also because production of C₂₋₄ may be forced by FTS at high temperatures, as mentioned earlier.

Table 6.14 Effect of temperature on overall liquid production rates from the base catalyst and the separate-bed (0.5 g of base catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor pressure = 300 psi, TOS = 24 – 48 h)

Temperature (°C)	280		300		320	
Bed arrangement	Base catalyst	Separate-bed	Base catalyst	Separate-bed	Base catalyst	Separate-bed
ZSM-5 weight (g)	0	0.5	0	0.5	0	0.5
Hydrocarbon production rate (g/kg FT cat./h)	237.50	271.10	466.67	615.63	400.00	481.68
Alcohol production rate (g/kg FT cat./h)	41.36	3.51	126.32	0.45	128.00	0.43

From Table 6.14, the alcohol rate for the base catalyst increases with increase in temperature, and the trend is consistent with the results of Ma et al. (2007b). The alcohol rates in the separate bed decrease with increasing temperatures because of the increased reaction rate forming hydrocarbons and water over ZSM-5. Even the lowest temperature is sufficient to convert nearly all the alcohols in the separate bed.

6.2.4.5 Hydrocarbons distribution in organic liquid phase

Table 6.15 shows the amounts of paraffins in the hydrocarbon liquid phase. The amounts of n-C₅ to C₁₂ are higher than n-C₁₃₊ for both the base catalyst and the separate bed at all temperatures. This means that the rates of cracking of n-C₁₃₊ (over ZSM-5) and the rates of FT reaction forming these compounds (over the base catalyst) are higher than those for the formation reactions of n-C₁₃₊. Therefore, E_{act} for reactions involving n-C₁₃₊ and FT reaction forming n-C₅ to C₁₂ might be higher than those for forming n-C₁₃₊.

Table 6.15 Effect of temperature on liquid paraffins from the base catalyst and the separate-bed (0.5 g of base catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor pressure = 300 psi, TOS = 24-48 h)

Temperature (°C)	280		300		320	
Bed arrangement	Base catalyst	Separate-bed	Base catalyst	Separate-bed	Base catalyst	Separate-bed
ZSM-5 weight (g)	0	0.5	0	0.5	0	0.5
n-paraffins	mg carbon/day					
n-C ₅	4	27	46	104	7	867
n-C ₆	20	155	235	271	50	2036
n-C ₇	55	165	264	171	90	1745
n-C ₈	65	85	334	73	125	674
n-C ₉	13	71	255	60	114	345
n-C ₁₀	49	56	176	56	94	556
n-C ₁₁	43	15	129	30	82	344
n-C ₁₂	39	9	94	22	73	102
Sum of n-C ₅ to n-C ₁₂	288	583	1533	787	635	6699
n-C ₁₃₋₂₂	30	19	318	50	180	160
i-paraffins	mg carbon/day					
i-C ₅	61	101	606	129	147	87
i-C ₆	76	49	193	149	168	204
i-C ₇	238	460	538	867	407	175
i-C ₈	287	508	608	803	461	67
i-C ₉	304	339	337	528	374	34
i-C ₁₀	179	238	225	493	301	56
i-C ₁₁	149	136	151	234	240	34
i-C ₁₂	114	80	100	278	184	10
Sum of i-C ₅ to i-C ₁₂	1408	1911	2758	3481	2282	667
i-C ₁₃₋₂₂	150	56	355	110	200	17
C ₂₃₊	180	5	40	20	60	12

Between 280-300°C, the amount of n-C₅₋₁₂ increases by a factor of approximately 5 in the base catalyst but increases by only a factor of approximately 1.5 in the separate bed. The rates of reactions involving cracking of n-C₅₋₁₂ (to small-chain species) over ZSM-5 increase more than the rates of FT reactions forming these species. Therefore, the activation energies for cracking reactions involving n-C₅₋₁₂ over ZSM-5 are higher than those for the formation reactions for these species. The amount of n-C₁₃₋₂₂

increases by a factor of approximately 10 in the base catalyst but increases by only approximately 2.5 in the separate bed. The greater extent of increases in the base catalyst is due to higher FTS activity at higher temperatures. The rates of reactions involving cracking of $n\text{-C}_{13-22}$ over ZSM-5 increase more than the rates of FT reactions forming these species. Therefore, the activation energies for cracking reactions involving $n\text{-C}_{13-22}$ over ZSM-5 are higher than those for the formation reactions of these species. The amount of $i\text{-C}_{5-12}$ increases by a factor of approximately 2 in the base catalyst and increases by approximately 1.5 in the separate bed. Also, the amount of $i\text{-C}_{13-22}$ increases by a factor of approximately 2.5 in the base catalyst and increases by approximately 2 in the separate bed. The lower extent of increase in the separate bed is because ZSM-5 rearranges all these species to form smaller-chain and aromatic molecules through cracking and aromatization reactions respectively. Therefore, the activation energies for cracking and aromatization reactions involving $i\text{-C}_{5-22}$ over ZSM-5 are higher than those for the formation reactions of these species.

Between 300-320°C, the amounts of $n\text{-C}_{5-12}$ and $i\text{-C}_{13-22}$ both drop by a factor of approximately 0.5 in the base catalyst. The lower extent of drop in the base catalyst is due to shift in the product spectrum towards small-chain molecules at higher temperature, as mentioned earlier. In the separate bed, the amount of $n\text{-C}_{5-12}$ increases by a factor of 10 and the amount of $i\text{-C}_{5-12}$ decreases by a factor of 0.2. The relatively greater extent of increase of $n\text{-paraffins}$ in the separate bed is because the rates of cracking reactions involving $i\text{-C}_{5-12}$ over ZSM-5 are higher than those for the formation reactions of $n\text{-C}_{5-12}$ over the base catalyst (isomers are more reactive than $n\text{-paraffins}$). Therefore, the activation energies for cracking reactions involving $i\text{-C}_{5-12}$ over ZSM-5 are higher than those for the formation reactions of $n\text{-C}_{5-12}$. The amounts of $i\text{-C}_{5-12}$ are nearly the same in the base catalyst, and there is not much effect on rates of formation of these species. Also, the amount of $i\text{-C}_{13-22}$ between 300-320°C drops by factor of approximately 0.5 in the base catalyst and drops by a factor of approximately 0.1 in the separate bed. Note that these drops are not consistent with those of trends between 280-300°C. The amounts of C_{23+} are relatively small compared to the amounts of all the other products.

Table 6.16 shows the distribution of the aromatic components with change in temperature. The amounts for the base catalyst are zero at all temperatures, because FTS provides no aromatics. But this is not true with the separate bed, where ZSM-5 provides the sites necessary for aromatic compound formation. The amounts of all aromatic compounds increase from 280 to 300°C. The increase is greater for toluene and least for butyl benzene, probably due to steric hindrance. A further increase in

temperature causes these amounts to decrease, probably because of coke deposition on ZSM-5 (Guanjie et al., 2010) reducing the aromatization activity of ZSM-5. The decrease is the least for butyl benzene and the greatest for toluene.

Table 6.16 Effect of temperature on aromatic compounds from the base catalyst and the separate-bed (0.5 g of base catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor pressure = 300 psi, TOS = 24 - 48 h)

Temperature (°C)	280		300		320	
Bed arrangement	Base catalyst	Separate-bed	Base catalyst	Separate-bed	Base catalyst	Separate-bed
ZSM-5 weight (g)	0	0.5	0	0.5	0	0.5
Compounds	mg carbon/day					
toluene	0	31	0	462	0	162
p-xylene	0	99	0	737	0	367
propyl benzene	0	99	0	563	0	306
butyl benzene	0	33	0	90	0	70

6.2.4.6 Alcohols and water in aqueous liquid phase

From Table 6.17, the total amount of alcohols for the base catalyst increases with increase in the temperature and the trend is consistent with the results of Ma et al. (2007b). Between 280-300°C, the total alcohol production increases by a factor of 3. Individually, ethanol, which is present in the largest amounts, increases by a relatively small amount, a factor of approximately 2.5. 1-pentanol, present in very small amount, increases by a factor of approximately 4. Between 300-320°C, the increases are much lower, probably due to deactivation.

From Table 6.17, the total alcohol amounts in the separate bed are vanishingly low compared to the base catalyst. ZSM-5 has the ability to convert almost all the alcohols formed by the base catalyst to hydrocarbon and water, and the alcohol amount decreases with increase in the temperature. At all temperatures, 2-propanol is the most abundant species. This means that the activation energies for the conversion of alcohol to hydrocarbon and water on ZSM-5 are higher than those for alcohols formation on the base catalyst. It can also be seen that even the lowest temperature is sufficient to convert nearly all the alcohol in the separate bed.

Table 6.17 Effect of temperature on weights of alcohols and water from the base catalyst and the separate-bed (0.5 g of base catalyst, 0.5 g of ZSM-5, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor pressure = 300 psi, TOS = 24 - 48 h)

Temperature (°C)	280		300		320	
Bed arrangement	Base catalyst	Separate-bed	Base catalyst	Separate-bed	Base catalyst	Separate-bed
ZSM-5 weight (g)	0	0.5	0	0.5	0	0.5
Compounds	Weights in aqueous phase (mg)					
methanol	73	2	243	0	307	0
ethanol	192	5	516	2	595	0
2-Propanol	36	35	92	5	115	5
1-Propanol	89	0	272	0	275	0
2-Butanol	14	2	31	0	26	0
1-Butanol	58	0	205	0	134	0
2-Pentanol	0	0	0	0	0	0
1-Pentanol	35	0	157	0	83	0
Total alcohols	496	42	1516	7	1536	5
Water	354	1458	894	2295	1664	1496

CHAPTER 7

CATALYST STABILITY TESTS

7.1 Conversions

Stability tests of the base catalyst along with 0.5 g of ZSM-5 have been carried out for 240 h time on stream (TOS) in the separate-bed catalyst arrangement. Figure 7.1 shows the CO and H₂ conversions. The CO and H₂ conversions start with low values, and then reach their maximum values in approximately 28 h. The catalyst seems stable up to 115 h, and then starts losing its activity slowly up to the end of the run, at 240 h. This general behavior confirms the use of the products obtained in the period from 24 – 48 h TOS to characterize the performance of the various catalysts and bed arrangements.

Figure 7.1 CO and H₂ conversions (%) with time on stream (TOS, h). Separate-bed catalyst arrangement, 0.5 g of base catalyst, 0.5 g of ZSM-5 catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 psi, TOS = 0 – 240 h.

The decrease in catalytic activity can be explained as follows. As discussed in Section 4.3, the base catalyst has FeO and Fe₃O₄ before starting the reaction. After starting the reaction, there might be rapid phase transformation of the iron oxide to the iron carbide, and the fraction of the iron carbide could increase rapidly in the initial reaction period. According to Davis (2009), the iron carbide shows

greater activity towards FT reactions. This could account for the rapid increase in the conversions in Figure 7.1 from 0 to 28 h. Davis (2009) also suggests that there is a decline in the iron-carbide phase with greater operating time. So the slow decline in the conversions in Figure 7.1 after 28 h may be due to a decline in the iron-carbide phase. ZSM-5 has no role in the conversion of syngas.

Figure 7.2 gives the amounts of CO₂ formed and CO unreacted with reaction time. There is not much change in CO₂ formed after 48 h TOS. This means that the combined effect of the base catalyst and ZSM-5 in the separate-bed catalyst arrangement is nearly constant. The slight increase in unreacted CO is due to the slow drop in CO conversion after 48 h, as also seen in Figure 7.1.

Figure 7.2 CO₂ and unreacted CO (g carbon/day) with time on stream (TOS, h). Separate-bed catalyst arrangement, 0.5 g of base catalyst, 0.5 g of ZSM-5 catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 psi, TOS = 0 - 240 h.

7.2 WGS and FTS reaction rates

The WGS and FTS rates are shown in Table 7.1. There is not much variation in WGS reaction activity. Therefore addition of ZSM-5 to the base catalyst in the separate-bed arrangement is inactive towards WGS reaction. Mahay et al. (1987) also confirm that ZSM-5 zeolite alone cannot show any activity towards WGS reaction. The FTS rate decrease slowly with time. This is because of the slow decline in FTS activity of the base catalyst, as explained in Section 7.1.

Table 7.1 WGS and FTS reaction rates with time on stream (TOS, h) (separate-bed catalyst arrangement, 0.5 g of base catalyst, 0.5 g of ZSM-5 catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 psi, N_{CO, inlet} = 2.112 mmole/min, TOS = 0 - 240 h)

TOS (h)	24-48	48-96	96-144	144-192	192-240
Rates	mmole/min				
rWGS= rCO ₂	0.84	0.86	0.86	0.84	0.86
rFTS = -rCO - rWGS	1.02	1.01	0.95	0.97	0.95

7.3 Gas analysis

From Figure 7.3, the amounts of all the gases are relatively constant after around 48 h, except for a spike at 240 h for C₃H₈. The increases are mainly due to a progressive shift in the product spectrum of the base catalyst towards lighter compounds (Botes et al., 2004), assuming that the cracking ability of the ZSM-5 catalyst is unchanged with time on stream.

From Figure 7.4, the amounts of C₃H₆, 1-C₄H₈, t-C₄H₈, c-C₄H₈, and C₅-olefins increase with reaction time. ZSM-5 has the ability to oligomerize these compounds (Borges et al., 2007; Knifton et al., 1994). The increase may be due to a decrease in oligomerization sites on ZSM-5, as well as a progressive shift in the product spectrum of the base catalyst towards lighter compounds (Botes et al., 2004).

Figure 7.3 Gas-phase n-paraffins detected by FID (g carbon/day) with time on stream (TOS, h). Separate-bed catalyst arrangement, 0.5 g of base catalyst, 0.5 g of ZSM-5 catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 psi, TOS = 0 - 240 h.

Figure 7.4 FID gases not shown in Figure 7.3 (g carbon/day) with time on stream (TOS, h). Separate-bed catalyst arrangement, 0.5 g of base catalyst, 0.5 g of ZSM-5 catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 psi, TOS = 0 - 240 h.

From Figure 7.5, the amounts of $i\text{-C}_4\text{H}_{10}$, $i\text{-C}_4\text{H}_8$, and $i\text{-C}_5\text{H}_{12}$ initially increase, then decrease with reaction time. It may be that there is a decrease in the number of isomerization sites on ZSM-5, due to coke deposition. Coke deposition on ZSM-5 could also account for (a portion of) the increase in Figure 7.3 and 7.4, along with the shift on the product spectrum of the FT catalyst. The presence of coke on ZSM-5 is further confirmed by EDX analysis of ZSM-5, as shown in Section 8.2.

Figure 7.5 FID gases not shown in Figure 7.3 and Figure 7.4 (g carbon/day) with time on stream (TOS, h). Separate-bed catalyst arrangement, 0.5 g of base catalyst, 0.5 g of ZSM-5 catalyst, Si/Al ratio in ZSM-5 = 50, H_2/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C , reactor pressure = 300 psi, TOS = 0 - 240 h.

7.4 Overall liquid hydrocarbon production rates

Overall liquid hydrocarbon production rates are shown in Figure 7.6. There is a slow decrease in production from 96 h onwards. The decrease in production can be explained by the increase in gas-phase light hydrocarbons by a shift in the product spectrum of the FT catalyst (Botes et al., 2004).

Figure 7.6 Liquid hydrocarbon production rate (g/Kg FT cat./h) with time on stream (TOS, h). Separate-bed catalyst arrangement, 0.5 g of base catalyst, 0.5 g of ZSM-5 catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 psi, TOS = 0 - 240 h.

7.5 Hydrocarbons distribution in organic liquid phase

Detailed liquid distribution of the hydrocarbons is shown in Appendix F.4. Table 7.2 gives information about the amounts of hydrocarbons distributed in the organic liquid phase. The amounts of n-C₅₋₁₂ increase with reaction time, while i-C₅₋₁₂ has a maximum at 96-144 h. The amounts of i-C₅₋₁₂ drop probably because of the reduced isomerization ability of ZSM-5 due to formation of coke with time. The amounts of C₇₋₁₀ aromatics, n-C₁₃₊, and i-C₁₃₊ decrease with reaction time. The decrease in amounts of C₁₃₊, both n- and i-, is also explained by the increase in gas-phase light hydrocarbons due to a shift in the product spectrum of the base catalyst. The decrease in the amounts of C₇₋₁₀ aromatics can be explained by coke deposition on the ZSM-5.

Table 7.2 Hydrocarbons distribution (g carbon/day) with time on stream (TOS, h) (separate-bed catalyst arrangement, 0.5 g of base catalyst, 0.5 g of ZSM-5 catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 psi, TOS = 0 - 240 h)

TOS (h)	24-48	48-96	96-144	144-192	192-240
Products	g carbon / day				
n-C ₅₋₁₂	1.19	1.48	1.63	1.67	1.86
i-C ₅₋₁₂	4.93	5.77	6.27	5.91	5.65
C ₇₋₁₀ Aromatics	1.91	1.21	0.53	0.39	0.34
Sum of C ₅₋₁₂	8.03	8.46	8.43	7.97	7.85
n-C ₁₃₊	0.06	0.02	0.01	0.01	0.01
i-C ₁₃₊	0.28	0.12	0.09	0.08	0.05
Sum C ₁₃₊	0.34	0.14	0.10	0.09	0.06

Figure 7.7 shows the amounts of individual aromatic compounds with increase in reaction time. The amounts of all the aromatic compounds increase for the first 48 h, decrease thereafter and level off after 144 h. ZSM-5 might be active for aromatization in the first 48 h. Coke deposition on the ZSM-5 pores causes the amounts of all the aromatic compounds to decrease with reaction time after 48 h.

Figure 7.7 Aromatics compounds (g carbon/day) with time on stream (TOS, h). Separate-bed catalyst arrangement, 0.5 g of base catalyst, 0.5 g of ZSM-5 catalyst, Si/Al ratio in ZSM-5 = 50, H_2/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 psi, TOS = 0 - 240 h.

7.6 Overall alcohol production rates

From Figure 7.8, the overall alcohol production rate drops somewhat till 96 h and increases slowly thereafter. The decrease in production is due to the ability of ZSM-5 to convert alcohols to hydrocarbons initially. Coke deposition probably reduces the ability of ZSM-5 to convert alcohols to hydrocarbons eventually, and hence alcohol production rate increases after 96 h.

Figure 7.8 Alcohol production rate (g/Kg FT cat./h) with time on stream (TOS, h). Separate-bed catalyst arrangement, 0.5 g of base catalyst, 0.5 g of ZSM-5 catalyst, Si/Al ratio in ZSM-5 = 50, H_2/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 psi, TOS = 0 - 240 h.

7.7 Alcohol distribution in the aqueous liquid phase

Table 7.3 shows the amounts of different alcohols for the separate-bed catalyst arrangement for reaction time until 240 h. The total amount for all the alcohols is small. Initially, 1-propanol is the most abundant species. At the largest TOS values, 1-butanol and 1-pentanol are the most abundant. But all the numbers are small and subject to error.

Table 7.3 Aqueous-phase compounds with time on stream (TOS, h) (separate-bed catalyst arrangement, 0.5 g of base catalyst, 0.5 g of ZSM-5 catalyst, Si/Al ratio in ZSM-5 = 50, H₂/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 psi, TOS = 0 - 240 h)

TOS (h)	24-48	48-96	96-144	144-192	192-240
Compounds	Weights in aqueous phase (mg)				
Methanol	0	3	6	8	2
Ethanol	1	2	2	16	0
2-Propanol	5	5	0	2	3
1-Propanol	12	2	0	0	6
2-Butanol	7	2	5	4	2
1-Butanol	0	0	0	0	12
2-Pentanol	5	0	5	6	10
1-Pentanol	2	0	2	2	12
Sum of Alcohols	31	14	20	39	46
Water	2269	2306	2230	2081	1914

The overall reaction sequence for the separate bed with TOS does not seem change with reaction time except that the coke deposition reduces ability of cracking, oligomerization, isomerization, and conversion of alcohols to hydrocarbons reactions on ZSM-5. The overall reaction sequence is also can be seen in Figure 6.8.

CHAPTER 8

CATALYST CHARACTERIZATION AFTER REACTION

8.1 EFFECT OF BED ARRANGEMENT ON ENERGY-DISPERSIVE X-RAY SPECTROSCOPY OF SPENT CATALYST

It was difficult to separate out ZSM-5 particles from quartz chips, and so Energy Dispersive X-Ray Spectroscopy (EDX) of only the spent ZSM-5 with 0.5 g ZSM-5 was done. Samples from both the separate-bed and mixed-bed arrangements were used.

Figure 8.1 shows EDX analysis of spent ZSM-5 in the separate bed after 72 h. As mentioned for Figure 4.4, Au and Pd are the coating metals used for EDX analysis and have nothing to do with our reaction data analysis. As previously discussed for Figure 4.4, the concentration of carbon (in the form of coke) for the unused ZSM-5 sample is zero. Figure 8.1 confirms the presence of carbon in the form of coke. This coke might be due to heavy and waxy hydrocarbon from the base catalyst. Note that the ZSM-5 sample after 72 h does not contain Fe and Cu metals. Hence there is no metal migration from the base catalyst in the separate bed.

Figure 8.1 EDX elemental analysis of spent ZSM-5 after 72 h (separate-bed catalyst arrangement, 0.5 g of base catalyst, 0.5 g of ZSM-5 catalyst, Si/Al ratio in ZSM-5 = 50, H_2/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 psi, TOS = 0 - 72 h)

Figure 8.2 shows EDX analysis of spent ZSM-5 in the mixed bed after 72 h. Figure 8.2 confirms the presence of carbon as well as Fe and Cu metals. The higher concentration of carbon relative to Figure 8.1 signifies a greater amount of coke deposition. The presence of metals in ZSM-5 suggests that metal migrates from FT catalyst to ZSM-5. Hence the base catalyst probably shows a declining activity towards reactions in the mixed bed, as discussed in Section 6.2.2.2.

Figure 8.2 EDX elemental analysis of spent ZSM-5 after 72 h (mixed-bed catalyst arrangement, 0.5 g of base catalyst, 0.5 g of ZSM-5 catalyst, Si/Al ratio in ZSM-5 = 50, H_2/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 psi, TOS = 0 - 72 h)

8.2 ENERGY-DISPERSIVE X-RAY SPECTROSCOPY AFTER CATALYST STABILITY TESTS

Only the ZSM-5 sample in the separate-bed arrangement using 0.5 g ZSM-5 was used. The EDX analysis of the spent ZSM-5 sample after 240 h of reaction is shown in Figure 8.3. Figure 8.3 shows the presence of carbon for ZSM-5 sample. As the reaction time increases, coke deposits on the ZSM-5 surface and ZSM-5 activity for isomerization declines. Note that the ZSM-5 sample after 240 h does not contain Fe and Cu metals, and hence there is no metal migration from the base catalyst in the separate bed.

Figure 8.3 EDX elemental analysis of ZSM-5 after 240 h (separate-bed catalyst arrangement, 0.5 g of base catalyst, 0.5 g of ZSM-5 catalyst, Si/Al ratio in ZSM-5 = 50, H_2/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 psi, TOS = 0 - 240 h)

8.3 COMPARISON OF SPENT SAMPLES

EDX samples discussed in Section 8.1 and Section 8.2 are compared here. If we compare Figure 8.1 and Figure 8.2, the concentrations of Si are same, but the concentrations of carbon and oxygen in the mixed bed are significantly higher than in the separate bed. The significant amount of carbon in the mixed bed might be due to the coke deposition on ZSM-5. The higher concentration of oxygen in the mixed bed is probably due to disintegration of the ZSM-5 pentasil unit framework in this configuration, and it might attract more water molecules.

From Figure 8.1 and Figure 8.3, the concentrations of Si are same. The concentrations of carbon and oxygen in the separate bed with 240 h TOS are significantly higher than in the separate bed with 72 h TOS. Hence, coke deposition on the ZSM-5 surface increases with time. The higher concentration of oxygen in the ZSM-5 sample of the separate bed with 240 h TOS is probably due to the increased disintegration of the pentasil unit framework with time.

As seen from Figure 8.1 and Figure 8.2, the ZSM-5 sample of the separate bed after 72 h TOS does not contain Fe and Cu metals, as opposed to the sample from the mixed bed. Hence there is metal migration from the base catalyst in the mixed bed.

CHAPTER 9

CONCLUSIONS

The conclusions that can be drawn on the data obtained are as follows.

1. Addition of ZSM-5 to the iron-based FT catalyst alters the product distribution towards the formation of gasoline-range i-paraffins and aromatics through the cracking of long-chain hydrocarbons and isomerization of n-paraffins, oligomerization of olefins and the formation of aromatics through aromatization reactions occurring on the ZSM-5 active sites.
2. The separate bed shows high activity towards FTS, and gives higher conversions and larger amounts of high-octane gasoline-range hydrocarbons. WGS and FTS rates are constant for increasing ZSM-5 in the separate-bed arrangement, probably because ZSM-5 is inactive towards CO consumption. The mixed-bed arrangement shows lower activity towards FTS and WGS compared to the separate bed. This may be due to lowering of the alkali content of the iron catalyst because of alkali migration to ZSM-5. EDX analysis of the spent ZSM-5 after 72 h shows metal migration from the base catalyst to ZSM-5 in the mixed bed, but not in the separate bed. Both the separate bed and the mixed bed show conversion of alcohols to hydrocarbons and water. The extent of conversion of alcohols is higher in the separate bed compared to the mixed bed. This is possibly because all alcohols pass over all the ZSM-5 in the separate bed, and so more amounts are reacted.
3. For the separate bed, the amounts of gas n- and i-paraffins increase with an increase in ZSM-5, probably because of enhanced cracking reactions. The amounts of olefins in the gas generally decrease with an increase in ZSM-5, probably because of an increase in the oligomerization reactions on ZSM-5. Liquid hydrocarbon production rates increase for small amounts of ZSM-5 because it converts alcohols formed by the base catalyst to hydrocarbons. Larger amounts of ZSM-5 provide additional cracking sites to give larger amounts of gas species. The production of alcohols decreases to nearly zero in the presence of even small amounts of ZSM-5. Heavier-chain hydrocarbon molecules (C_{13+}) formed by the base catalyst are effectively cracked and isomerized on the ZSM-5 catalyst surface. The base catalyst shows no selectivity towards aromatic compounds, but addition of ZSM-5 forms alkyl-benzene aromatic compounds (C_{7-10}).

p-xylene yields are highest, probably because of low steric hindrance compared to other aromatic compounds. 0.25 g ZSM-5 is sufficient to crack long-chain hydrocarbons, but not enough to give high yields of aromatic compounds.

4. For the mixed bed, FTS and WGS rates decrease with the addition of a small amount of ZSM-5, but then increase with an increase in ZSM-5, but these values are lower than those of the base catalyst. The amounts of gas n- and i-paraffins increase with an increase in ZSM-5, probably because of enhanced cracking reactions. The amounts of olefins in the gas generally decrease with a small amount of ZSM-5, probably because of an increase in the oligomerization reactions on ZSM-5. Further addition of ZSM-5 does not seem to contribute much towards oligomerization reactions. Liquid hydrocarbon production rates decrease with an increase in ZSM-5, possibly due to metal migration from the FT catalyst to ZSM-5. The low activity of physical mixtures of the base catalyst and ZSM-5 is also reported by Botes et al. (2004). As in the separate bed, ZSM-5 converts alcohols formed by the base catalyst to hydrocarbons, and larger amounts of ZSM-5 provide additional cracking sites to give larger amounts of gas species. However, for the mixed bed, the maximum amount of ZSM-5 is not sufficient to convert all the alcohols produced by the base catalyst. Heavier-chain hydrocarbon molecules (C_{13+}) formed by the base catalyst are effectively cracked and isomerized on the ZSM-5 catalyst surface. As in the separate bed, the base catalyst shows no selectivity towards aromatic compounds, but addition of ZSM-5 forms alkyl-benzene aromatic compounds (C_{7-10}). The aromatic yield shows a maximum at 0.5 g ZSM-5, and higher amounts of ZSM-5 decrease the yield. 0.25 g ZSM-5 is sufficient to crack long-chain hydrocarbons but not enough to give high yields of aromatic compounds.
5. When comparing both the beds, it is seen that the maximum amount of i- C_{5-12} plus aromatics (high-octane gasoline-range hydrocarbons) is formed in the separate bed with 0.5 g ZSM-5.
6. The separate bed and mixed bed are quantitatively compared for increasing ZSM-5 using a delta terminology. There is no improvement (i.e., delta is negative) in the CO conversions, the WGS and FTS rates, the hydrocarbon production rate, i-paraffins production, and aromatic hydrocarbons production when the base catalyst and ZSM-5 are mixed, compared to separate-bed case. The conversion of alcohols to hydrocarbons and water is not complete in the mixed bed, as opposed to the separate bed.

7. The effect of increasing temperature on the product distribution is studied on the base catalyst and the separate bed. WGS and FTS rates are increased at 300°C, but higher temperatures do not seem to enhance these rates. The addition of ZSM-5 has a negligible contribution to FTS and WGS rates with increase in temperature. Production of small-chain hydrocarbons (C_{1-5}) increases with increase in temperature in the base catalyst because of higher FTS rates. In the gas phase, it is observed that the amounts of species with low carbon number (like CH_4) increase more than those with higher carbon number (like $n-C_5H_{12}$), probably because of higher activation energy for the formation of species with low carbon number. The increase in the amounts of these species (except gas olefins in general, which undergo oligomerization over ZSM-5) with temperature in the separate bed is because of combinations of reactions like higher FTS rates (due to the base catalyst), cracking (of long-chain molecules), and isomerization reactions. There is a greater increase of overall hydrocarbon liquid production rates between 280-300°C in the separate bed, compared to the base catalyst. This is because combinations of the reactions occurring on the both the base catalyst and ZSM-5 (FTS and WGS on the base catalyst, and conversion of alcohols to hydrocarbon, oligomerization, and aromatization occurring on ZSM-5). A further increase in temperature to 320°C could decrease the production rate because of increased cracking of long-chain hydrocarbons, and also because production of C_{1-4} may be dominated by FTS at high temperature. Between 280-300°C, it is found that the activation energies for cracking and aromatization reactions involving n - and i - C_{5-22} over ZSM-5 are greater than those for the formation reactions of these species. Further increase in temperature generally causes these species to crack to small-chain molecules. Aromatic yields are found to decrease, probably due to coke formation at 320°C. The total amount of alcohols for the base catalyst increases with increase in the temperature, and the trend is consistent with the results of Ma et al. (2007b). The extent of conversion of alcohols to hydrocarbons is not much changed with temperatures, and 280°C is sufficient for ZSM-5 to convert all the alcohols formed by the base catalyst.
8. A progressive loss of the activities of the base catalyst and the ZSM-5 occurs with increasing time on stream (TOS). The slow decline in activity of the base catalyst with TOS could be due to a decrease in iron carbide. EDX of spent ZSM-5 confirms that coke has deposited with TOS. A loss of ZSM-5 activity is because of the decline in the active sites due to coke formation.

Martinez et al. (2005) show similar results. The decline in liquid hydrocarbon production rate is partly due to increase in gas-phase hydrocarbons by a shift in the product spectrum of the FT catalyst and partly due to coke deposition on ZSM-5. The coke deposition of ZSM-5 decreases the formation of aromatic species due to declining aromatization sites. Coke deposition on ZSM-5 has a negligible effect on the ability of ZSM-5 to convert alcohols to hydrocarbons and water.

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APPENDICES

APPENDIX A

CHROMATOGRAPH OPERATING CONDITIONS FOR GAS AND LIQUID PRODUCTS

A.1 Chromatograph operating conditions for gas products

Gas chromatograph model: The PerkinElmer GC

Detector used: Thermal-conductivity detector (TCD) and Flame-ionization detector (FID)

Detector temperature TCD: 200 °C, Detector temperature FID: 250 °C

Carrier gas TCD: He , Carrier gas FID: N₂

Carrier gas inlet pressure: He: 33 psig, N₂: 14.1 psig

Carrier gas flow rate He: 40 ml/min

Carrier gas flow rate N₂: 30 ml/min

H₂ flow: 45 ml/min

Air flow: 450 ml/min

Columns used:

18" RGAP, 1/8" Sf

17' RGA20, 1/8" Sf

7' RGAP 1/8" Sf

7" RGA, 1/8" Sf

7' HayeSep N 1/8" Sf

9' Molecular Sieve 13x 1/8" Sf

9' Molecular Sieve, 1/8" Sf

4' HayeSep T, 1/8" Sf

Oven temperature: 60 °C

Period of analysis: 15 min

A.2 Chromatograph operating conditions for liquid products

Varian 3400 GC is used for liquid analysis. GC is equipped with auto injection setup which is operated by 30 Psig air.

Column used for hydrocarbon liquid analysis: J and W scientific DB 1 capillary column, length: 30 m, film thickness: 1.5 μ m.

Column used for aqueous liquid analysis: Restek packed column, TX-TA 80/100, length: 6 ft, ID: 2.00 mm, OD: 1/8 in, SILCO VAR 3400 PRECOND OC INV: 2 in, OUTV: 1.5 in

Table A.1 GC operating conditions for liquid analysis

Conditions	Hydrocarbon GC operating conditions (FID A)	Aqueous GC operating conditions (FID B)
Carrier gas used	Nitrogen	Nitrogen
Carrier gas inlet pressure (psig)	6	82
Period of analysis (min)	48	28
Column		
Initial column Temperature ($^{\circ}$ C)	50	50
Final column Temperature ($^{\circ}$ C)	290	300
Column initial hold time (min)	0	0
Column temperature rate ($^{\circ}$ C/min)	5	10
Injector		
Initial injection Temperature ($^{\circ}$ C)	200	200
Final injection Temperature ($^{\circ}$ C)	250	250
Injection hold time (min)	1	0
Injection temperature rate ($^{\circ}$ C/min)	10	10
Detector		
Detector temperature ($^{\circ}$ C)	300	300

APPENDIX B

CHROMATOGRAPH CALIBRATION PROCEDURE FOR GAS AND LIQUID PRODUCTS

B.1 Chromatograph calibration procedure for gas products

B.1.1 TCD calibration of gases

A slope of different compounds is calculated by plotting moles of compounds in 1 c.c. loop verses GC area. Relative response factor (rRF) is calculated based on the Equation (B.1). In Equation (B.1), $slope_X$ is refers to slope of unknown component listed in Table B.1. Internal standard as helium gas is used for Helium, Hydrogen, and carbon dioxide gas compounds. Internal standard as argon gas is used for argon, nitrogen, methane, and carbon monoxide gas compounds. In Equation (B.1), $slope_{He, Ar}$ refers to slopes of Helium or Argon depending on the internal standard definition for a particular gas component. Slopes and rRF values for TCD gases are given in Table B.1.

Definition of relative response factor with TCD: peak area of component: A; concentration: C

$$relative\ Response\ Factor\ of\ gas\ component\ X, (rRF)_X = \left(\frac{\frac{A_X}{C_X}}{\frac{A_{He,Ar}}{C_{He,Ar}}} \right) = \frac{slope_X}{slope_{He,Ar}} \quad \dots (B.1)$$

Table B.1 Slope and rRF of TCD gas compounds

Component	Slopes (Area/moles in 1 c.c.)	rRF
H ₂	3.18353E+11	1.222068
CO	3.43655E+11	0.950770
He	2.60503E+11	1.000000
Ar	3.61449E+11	1.000000
N ₂	3.21642E+11	0.889867
CO ₂	4.08774E+11	1.569168
CH ₄	2.77742E+11	0.768411

B.1.2 FID calibration of gases

A slope of different compounds is calculated by plotting moles of compounds in 1 c.c. loop verses GC area. Relative response factor is calculated based on the Equation (B.2). In Equation (B.2), $slope_X$ is refers to slope of unknown component listed in Table B.2. In Equation (B.2), $slope_{CH_4}$ refers to slopes of methane gas. Slopes and rRF values for FID gases are given in Table B.2.

Definition of relative response factor with FID: peak area of component: A; concentration: C

$$\text{relative Response Factor of gas component } X, (rRF)_X = \left(\frac{\frac{A_X}{C_{CH_4}}}{\frac{A_{CH_4}}{C_X}} \right) = \frac{slope_X}{slope_{CH_4}} \quad \dots (B.2)$$

Table B.2 Slope and rRF of FID gas compounds

Compounds	Slopes	rRF
CH ₄	1.68E+07	1.000000
C ₂ H ₆	3.17E+07	1.886435
C ₂ H ₄	3.17E+07	1.886435
C ₃ H ₈	4.71E+07	2.805648
C ₃ H ₆	4.55E+07	2.7124589
C ₃ H ₄	3.62E+07	2.1574558
i-C ₄ H ₁₀	6.09E+07	3.6304886
n-C ₄ H ₁₀	6.39E+07	3.8101614
1-C ₄ H ₈	6.02E+07	3.5872479
i-C ₄ H ₈	2.02E+07	1.2040752
t-C ₄ H ₈	5.72E+07	3.4097923
c-C ₄ H ₈	6.42E+07	3.8251059
1,3 C ₄ H ₆	5.97E+07	3.5566422
i-C ₅ H ₁₂	6.71E+07	3.9991299
n-C ₅ H ₁₂	4.97E+07	2.9605052
C ₅₊ (Gas)	9.96E+07	5.9329234

B.2 Chromatograph calibration procedure for liquid products

B.2.1 Chromatograph calibration procedure for organic liquid (oil) phase products

CS₂ is used as the solvent for oil product sample preparation. The straight-chain paraffins are identified by comparing retention times to standard D-2887 obtained from Restek. Branched paraffins are assumed to elute before the straight-chain paraffin with the same carbon number. A few other large peaks eluting between known paraffins were identified as toluene, p-xylene, n-propyl benzene and n-butyl benzene by using standard D-3710 obtained from Restek. However, this was the only aromatic standard we could obtain from Restek. Since the product is expected to contain other di-methyl benzenes and trimethyl benzenes, these were not identified and would have been counted as i-paraffins. Also the response factors for all the liquid hydrocarbons assumed to be linear and constant.

B.2.2 Chromatograph calculation procedure for aqueous phase products

Cyclohexanol as an internal standard and deionized-water as solvent are used for aqueous phase sample preparation. Retention times of alcohols were identified using Accustandard standard sample (PS-111 C Alcohols C₁-C₅ kit). Then each standard sample, for example methanol, is added to preknown quantity of cyclohexanol and water. Then this prepared sample is injected in the GC and areas are noted. Table B.3 represents areas and weights of standard samples. This table is useful in quantification of aqueous compounds. Quantification of aqueous compounds is described in section D.

Table B.3 Areas and weights of standard alcohol samples

Standard (x)	A _{x, standard}	A _{cyclohexanol, standard}	Wt _{cyclohexanol, standard} (μg)	Wt _{x, standard} (μg)
Methanol	84286	19451	22.2	383.7
Ethanol	82843	16693	18.3	225.6
2-Propanol	12534417	290032	5.8	816.1
1-Propanol	78959	16539	19.5	305.1
2-Butanol	31995228	1832669	34.2	796.5
1-Butanol	82482	18344	18.1	391.4
2-Pentanol	41499452	135882	21	783.9
1-Pentanol	77869	19888	18.8	388.3

APPENDIX C

MASS FLOW CONTROLLER CALIBRATION

The experimental setup, as shown Figure 3.1, has three lines for feed gas and each being controlled individually by a Brook's mass-flow controller (MFC). Calibration procedure of these MFC's is described below. Calibration for all these MFC's (hydrogen, helium and syngas mixture gases) follows the similar procedure. The gas flow rate is preset to minimum set value on the MFC and the system is allowed to attain steady state. The volumetric flow rate at the outlet is measured using bubble flow meter. Steady state of the system is assumed when constant outlet volumetric flow rates were achieved. The room temperature and pressure is also noted. The readings are then repeated similarly for other MFC set values and calibration curve is plotted. The calculations are given below.

Measured volumetric flow rate of gas = V_1 cc/min

Measured ambient temperature = T_1 K

Measured ambient pressure = P_1 mm Hg

Assuming ideal gas law holds for all the gas species. According to ideal gas law,

$$V_2 = \left(\frac{P_1}{P_2}\right) \times \left(\frac{T_2}{T_1}\right) \times V_1 \text{ (cc/min)} \quad \dots \text{ (C.1)}$$

Where,

V_2 = volume of the species in the loop at STP conditions

P_2 = pressure at STP conditions, 760 mm Hg

T_2 = temperature at STP conditions, 273 K

Figure C.1 MFC calibration curve for He gas

Figure C.2 MFC calibration curve for H₂ gas

Figure C.3 MFC calibration curve for syngas mixture gas (45 % CO, 45 % H₂, 5% Ar, 5% He)

APPENDIX D

CALCULATIONS FOR RESULTS WITH BASE CASE CATALYST AND ZSM-5 CATALYST

D.1 Calculation procedure for gas analysis

D.1.1 Calculation procedure for TCD gas analysis

Feed flow (mol/min) with TCD can be calculated as,

$$F_{X,out} \left(\frac{\text{mol}}{\text{min}} \right) = \frac{(A_{X,out})}{(A_{He,Ar,out}) \times (rRFx)} \times F_{He,Ar,in} \left(\frac{\text{mol}}{\text{min}} \right) \quad \dots (D.1)$$

Internal standard as helium is used for helium, hydrogen, and carbon dioxide gas compounds. Internal standard as argon gas is used for argon, nitrogen, methane, and carbon monoxide gas compounds.

The conversions are calculated as,

$$CO \text{ conversions } (\%) = 100 \times \frac{\text{mole rate of CO consumption}}{\text{mole rate of CO inlet}} \quad \dots (D.2)$$

$$H_2 \text{ conversions } (\%) = 100 \times \frac{\text{mole rate of H}_2 \text{ consumption}}{\text{mole rate of H}_2 \text{ inlet}} \quad \dots (D.3)$$

D.2.2 Calculation procedure for FID gas analysis

Feed flow (mol/min) with FID can be calculated as,

$$F_{X,out} \left(\frac{\text{mol}}{\text{min}} \right) = \frac{(A_{X,out})}{(A_{CH_4,out}) \times (rRFx)} \times F_{CH_4,out,TCD} \left(\frac{\text{mol}}{\text{min}} \right) \quad \dots (D.4)$$

D.2 Calculation procedure for liquid analysis

D.2.1 Calculation procedure for oil phase analysis

GC sample is prepared using CS₂ as a solvent. 200μl of CS₂ and 800μl of FT hydrocarbon liquid phase is taken in a 1-ml GC sample vial. Similarly other oil samples are prepared, and GC auto sampler injects 1μl per injection.

The response factors of the liquid hydrocarbons assuming to be linear and constant. Therefore we can calculate weight percentage of liquid hydrocarbons directly from GC areas.

$$\text{weight percentage of liquid hydrocarbon } x \text{ (wt}_x\%) = 100 \times \frac{\text{Area of hydrocarbon } x}{\text{Total area} - \text{Area of CS}_2} \dots \text{(D.5)}$$

$$\text{Actual weight of liquid hydrocarbon } x \text{ (g)} = \text{wt}_x\% \text{ of hydrocarbons} \times \text{oil weight collected (g)} / 100 \dots \text{(D.6)}$$

D.2.2 Calculation procedure for aqueous phase analysis

The internal standard is used to correct for sample volume variations. So we have to correct for sample volume variations by taking the ratio of all peak areas to the internal standard in both the sample and the standard. Since the internal standard has a known concentration in both the sample and the standard, it can be used to correct for variations. Since the concentrations of alcohols responsible for the standard peaks are known, this comparison will allow you to calculate a concentration from the sample peak areas.

Let's pick Methanol as an example:

In order to relate the Area of Methanol in sample to the area of Methanol in the standard, we must first correct for sample variations to arrive at a corrected area of Methanol.

$$A_{\text{corrected,Methanol}} = A_{\text{Methanol,sample}} \times \frac{(A_{\text{cyclohexanol,standard}})}{(A_{\text{cyclohexanol,sample}})} \times \frac{\text{wt}_{\text{cyclohexanol,sample}}}{\text{wt}_{\text{cyclohexanol,standard}}} \dots \text{(D.7)}$$

Now, we can calculate weight of methanol in GC vial from this corrected area of methanol.

$$\text{wt}_{\text{Methanol,in GC vial}} = A_{\text{corrected,Methanol}} \times \frac{\text{wt}_{\text{Methanol,standard}}}{A_{\text{Methanol,standard}}} \dots \text{(D.8)}$$

$A_{\text{Methanol, standard}}$ $A_{\text{cyclohexanol, standard}}$ $\text{wt}_{\text{cyclohexanol, standard}}$ (μg) $\text{wt}_{\text{Methanol, standard}}$ (μg) are provided in Table B.3.

The subscript 'sample' in equation (D.7) refers to GC vial sample.

Similar procedure is followed for other alcohols and weights of alcohols can be calculated. Now we know the weights of all the alcohols (g) in the GC vial. The weight of methanol in actual fishcer-tropsch aqueous sample can be calculated as,

$$\text{Methanol weight in Fischer-Tropsch aqueous sample} = \text{Weight of Aqueous weight collected in FT reaction (g)} \times \frac{\text{wt Methanol, in GC vial}}{\text{GC vial sample weight (g)}} \quad \dots \text{ (D.9)}$$

GC vial sample weight (g) is the sample weight in GC vial without cyclohexanol and water.

Similarly, weight of other alcohols in Fischer-Tropsch aqueous sample can be calculated and *sum of alcohols weight calculated in Fischer-Tropsch aqueous sample (g)* can be obtained. Water amount in Fischer-Tropsch aqueous sample can be calculated as,

$$\text{Water in Fischer-Tropsch sample (g)} = \text{Weight of Aqueous weight collected in FT reaction (g)} - \text{sum of alcohols weight calculated in Fischer-Tropsch aqueous sample (g)} \quad \dots \text{ (D.10)}$$

CATALYST PREPARATION CALCULATION PROCEDURE

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Project catalyst preparation

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Support 3 g of Norit SX Ultra - pore volume = 0.89 ml/g

Catalyst composition : 6 wt% Mo, 16 wt% Fe, 0.8 wt% Cu, 0.9 wt% K

$$6 \text{ wt\% Mo on AC} = 3 \times 6 \times 0.01 = 0.18 \text{ g on 3g of AC}$$

molecular weight of Ammonium Molybdate = 1235.86 g/mol

$$\text{molecular weight of Mo} = 95.94 \text{ g/mol}$$

$$\begin{aligned} 1235.8 \text{ g salt} &\leftrightarrow 95.94 \text{ g Mo} \\ ? &\leftrightarrow 0.18 \text{ g Mo desired} \\ = 0.18 \times \frac{1235.8}{95.94} &= 0.33 \text{ g Mo-salt} \end{aligned}$$

similarly other calculations are done. Results are tabulated below,

(wt%)	(g/mol)	(g/mol)	(g)	(ml/3 g of AC)
metal desired wt%	molecular wt of metal	molecular wt of salt	Amount of salt required	Maximum water required $= \text{wt. of support} \times \text{Pore volume}$
6 wt% Mo	95.94	1235.86	0.33	$3 \times 0.89 = 2.67$
16 wt% Fe	55.845	1604	3.47	2.67
0.8 wt% Cu	63.55	241.6	0.09	2.67
0.9 wt% K	39	101.1	0.07	2.67

Salts used :-

$$\text{Mo: } (\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$$

$$\text{Fe: } \text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$$

$$\text{Cu: } \text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$$

$$\text{K: } \text{KNO}_3$$

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Read and Understood By _____

R. Prakash

01/15/2011

Signed _____

Signed _____

Date _____

APPENDIX F.1

CONVERSIONS AND LIQUID WEIGHTS COLLECTED FOR BASE CATALYST, SEPARATE BED, AND MIXED BED ARRANGEMENT

Table F.1 Conversions and liquid weights collected for base catalyst, separate bed, and mixed bed

Bed arrangement	Base catalyst			Separate-bed					Separate-bed and catalyst testing TOS (h)					Mixed-bed		
ZSM-5 weight (g)	0	0	0	0.25	0.5	1	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.25	0.5	1
Base catalyst weight (g)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
TOS (h)	24-48	24-48	24-48	24-48	24-48	24-48	24-48	24-48	24-48	48-96	96-144	144-192	192-240	24-48	24-48	24-48
T(°C)	280	300	320	300	300	300	320	280	300	300	300	300	300	300	300	300
CO conversions (%)	42.2	81.3	88	85.8	88.2	85.9	84.6	44.7	81.3	84.3	84.4	83.2	80.2	52.2	58.9	76
H ₂ conversions (%)	32.1	54.9	63	56.5	65.6	60.7	60.6	28.8	56.6	59.5	58.1	54.5	53	33.9	36.4	49.3
Error in carbon balance (%)	-8.4	-1.3	-5.7	-4.9	1.7	-3.1	-5.9	-2.4	4.75	3.06	0.4	-0.9	-4.2	-7.6	1.3	4.5
Hydrocarbon organic liquid weight (g)	2.85	5.6	4.8	7.29	7.39	5.68	5.78	3.25	7.62	15.6	14.9	14.04	13.68	3.75	4.21	3.09
Aqueous weight (g)	0.85	2.41	3.2	2.40	2.30	2.50	1.50	1.50	2.3	4.64	4.5	4.24	3.92	1.20	1.50	2.30

APPENDIX F.2

WGS AND FTS REACTION RATES FOR ALL REACTIONS

Table F.2 WGS and FTS rates

Bed arrangement	Base catalyst			Separate-bed					Catalyst stability testing in separate-bed					Mixed-bed		
ZSM-5 weight (g)	0	0	0	0.25	0.5	1	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.25	0.5	1
Base catalyst weight (g)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Temperature (°C)	280	300	320	300	300	300	320	280	300	300	300	300	300	300	300	300
TOS (h)	24-48	24-48	24-48	24-48	24-48	24-48	24-48	24-48	24-48	48-96	96-144	144-192	192-240	24-48	24-48	24-48
	g carbon /day															
CO ₂	10.2	14.39	14.2	15.56	15.1	15.5	15.12	8.81	14.6	14.84	14.94	14.6	14.84	9.85	10.34	13.96
Unreacted CO	18.5	6.84	4.2	5.27	4.3	5.12	5.17	18.51	4.3	4.2	5.06	5.12	5.2	15.8 3	14.98	8.58
Rates	mmol/min															
N _{CO,inlet}	1.92	2.11	1.94	2	2.11	2.11	1.94	1.94	2.11	2.11	2.11	2.11	2.11	1.92	2.11	2.07
N _{CO,unreacted}	1.07	0.40	0.24	0.30	0.25	0.30	0.30	1.07	0.25	0.24	0.29	0.30	0.30	0.92	0.87	0.50
rCO ₂ = rWGS = N _{CO2}	0.59	0.83	0.82	0.90	0.87	0.90	0.88	0.51	0.84	0.86	0.86	0.84	0.86	0.57	0.60	0.81
(-rCO) = rFTS + rWGS = N _{CO,inlet} - N _{CO,unreacted}	0.85	1.72	1.70	1.70	1.86	1.81	1.64	0.87	1.86	1.87	1.82	1.81	1.81	1.00	1.24	1.57
rFTS = (-rCO) - rWGS	0.26	0.89	0.88	0.79	0.99	0.92	0.77	0.36	1.02	1.01	0.95	0.97	0.95	0.43	0.64	0.77

APPENDIX F.3

FID GAS REACTION DATA FOR BASE CATALYST, SEPARATE-BED, AND MIXED-BED ARRANGEMENT

Table F.3 FID gas amounts for base catalyst, separate bed, and mixed bed

Bed arrangement	Base catalyst			Separate-bed					Catalyst stability testing in separate-bed					Mixed-bed		
ZSM-5 weight (g)	0	0	0	0.25	0.5	1	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.25	0.5	1
Base catalyst weight (g)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
T(°C)	280	300	320	300	300	300	320	280	300	300	300	300	300	300	300	300
TOS (h)	24-48	24-48	24-48	24-48	24-48	24-48	24-48	24-48	24-48	48-96	96-144	144-192	192-240	24-48	24-48	24-48
Compounds	g carbon/day															
CH ₄	0.7200	2.3114	3.2254	1.9456	2.2100	2.8100	3.7913	0.8887	2.1200	2.2100	2.4000	2.8200	2.9800	1.1975	1.3400	2.2739
C ₂ H ₆ + C ₂ H ₄	0.6500	1.7593	2.2115	1.7200	1.6700	1.2992	1.9219	0.4534	1.5200	1.6100	1.7100	2.4100	2.4600	0.8414	0.7784	0.7200
C ₃ H ₈	0.2100	0.4963	0.5619	0.6985	1.4868	2.3983	1.6100	0.4566	0.9200	0.9600	1.0200	1.0600	1.1000	0.3789	0.5004	1.1788
C ₃ H ₆	0.6400	2.1351	2.6364	0.2974	0.1059	0.0107	0.2058	0.0999	0.3800	0.4100	0.4200	0.4600	0.5100	0.7105	0.6038	0.5800
i-C ₄ H ₁₀	0.0000	0.0263	0.0319	0.4649	1.0322	1.8350	1.1200	0.2943	0.1100	0.3200	0.4760	0.5500	0.7500	0.2430	0.4626	0.9126
n-C ₄ H ₁₀	0.1800	0.3571	0.3696	0.5051	1.0385	1.3937	1.1100	0.3196	0.4100	0.6600	0.8100	0.8500	1.4900	0.2653	0.3599	0.6686
1-C ₄ H ₈	0.9000	1.1064	1.3653	0.0670	0.0142	0.0000	0.1356	0.0596	0.6500	0.6300	0.6100	0.5700	0.6300	0.2300	0.2152	0.1438
i-C ₄ H ₈	0.0000	0.0000	0.0000	1.3390	0.5800	0.0099	0.7678	0.4431	0.1000	0.1800	0.2600	0.3100	0.3900	0.7450	0.6678	0.4211
t-C ₄ H ₈	0.1900	0.2415	0.2456	0.1974	0.1000	0.0000	0.1166	0.0810	0.0200	0.0600	0.0240	0.0900	0.0000	0.2371	0.1566	0.1540
c-C ₄ H ₈	0.0000	0.0000	0.0000	0.1238	0.0198	0.0000	0.0745	0.0480	0.5600	0.8600	1.1500	1.2800	1.2600	0.1628	0.1084	0.0900
i-C ₅ H ₁₂	0.0000	0.0321	0.0373	0.3658	0.7832	1.0683	0.8100	0.2652	0.5800	0.3800	0.2600	0.1800	0.1100	0.2223	0.3731	0.6460
n-C ₅ H ₁₂	0.2100	0.3342	0.2964	0.3754	0.4100	0.5444	0.4300	0.2652	1.0300	0.6800	0.2300	0.1500	0.0900	0.2074	0.2551	0.3495
C ₅ -gas	0.9100	1.1972	1.2505	0.9441	0.5568	0.4186	0.8300	0.5100	0.7800	0.4600	0.1700	0.1400	0.1000	0.9646	0.8444	0.7167

APPENDIX F.4

ORGANIC AND AQUEOUS PHASE REACTION DATA FOR BASE CATALYST, SEPARATE-BED, AND MIXED-BED ARRANGEMENT

Base case catalyst at T=280°C Base catalyst weight = 0.5 g, ZSM-5 weight = 0 g, H ₂ /CO ratio = 1, total feed rate = 100 scc/min, reactor pressure = 300 psi, TOS = 24-48 h, Organic phase wt = 2.85 g, Aqueous phase wt = 0.85 g							
Aromatics	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
toluene	0	0	7	92	0	0	0
p-xylene	0	0	8	106	0	0	0
propyl-benzene	0	0	9	120	0	0	0
butyl-benzene	0	0	10	134	0	0	0
n-praffins	wt % in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	sum mmol/min	0 g carbon /day
n-C ₅	0.1085	0.0031	5	44	0.0001	0.0000	0.0042
n-C ₆	0.8366	0.0238	6	86	0.0003	0.0002	0.0200
n-C ₇	2.3155	0.0660	7	100	0.0007	0.0005	0.0554
n-C ₈	2.7204	0.0775	8	114	0.0007	0.0005	0.0653
n-C ₉	0.5511	0.0157	9	128	0.0001	0.0001	0.0133
n-C ₁₀	2.0517	0.0585	10	142	0.0004	0.0003	0.0494
n-C ₁₁	1.8003	0.0513	11	156	0.0003	0.0002	0.0434
n-C ₁₂	1.6135	0.0460	12	170	0.0003	0.0002	0.0390
n-C ₁₃	1.4729	0.0420	13	184	0.0002	0.0002	0.0356
n-C ₁₄	0.3435	0.0098	14	198	0.0000	0.0000	0.0083
n-C ₁₅	1.2709	0.0362	15	212	0.0002	0.0001	0.0308
n-C ₁₆	1.1789	0.0336	16	226	0.0001	0.0001	0.0285
n-C ₁₇₊	7.2391	0.2063	17	240	0.0009	0.0006	0.1754
						Sum in oil	0.5686
i-paraffins	wt % in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
i-C ₅	1.5742	0.0449	5	44	0.0010	0.0007	0.0612
i-C ₆	3.2011	0.0912	6	86	0.0011	0.0007	0.0764
i-C ₇	9.9438	0.2834	7	100	0.0028	0.0020	0.2381
i-C ₈	11.9565	0.3408	8	114	0.0030	0.0021	0.2870
i-C ₉	12.6515	0.3606	9	128	0.0028	0.0020	0.3042
i-C ₁₀	7.4179	0.2114	10	142	0.0015	0.0010	0.1787
i-C ₁₁	6.1832	0.1762	11	156	0.0011	0.0008	0.1491
i-C ₁₂	4.7213	0.1346	12	170	0.0008	0.0005	0.1140
i-C ₁₃	3.6265	0.1034	13	184	0.0006	0.0004	0.0876
i-C ₁₄	4.1313	0.1177	14	198	0.0006	0.0004	0.0999
i-C ₁₅	1.7895	0.0510	15	212	0.0002	0.0002	0.0433
i-C ₁₆	1.3616	0.0388	16	226	0.0002	0.0001	0.0330
i-C ₁₇₊	7.5755	0.2159	17	240	0.0009	0.0006	0.1835
						Total in oil	2.4243
Alcohols	wt % in aqueous liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
Methanol	8.6000	0.0731	1	32	0.0023	0.0016	0.0274
Ethanol	22.6000	0.1921	2	46	0.0042	0.0029	0.1002
2-Propanol	4.2000	0.0357	3	60	0.0006	0.0004	0.0214
1-Propanol	10.5000	0.0893	3	60	0.0015	0.0010	0.0536
2-Butanol	1.6000	0.0136	4	74	0.0002	0.0001	0.0088
1-Butanol	6.8000	0.0578	4	74	0.0008	0.0005	0.0375
2-Pentanol	0.0000	0.0000	5	88	0.0000	0.0000	0.0000
1-Pentanol	4.1000	0.0349	5	88	0.0004	0.0003	0.0238
Water	41.6000	0.3536	0	18	0.0196	0.0136	0.0000
						Total in Aqueous	0.2453
Total carbon due to oil and Aqueous phase			2.6696 g carbon /day				

Base case catalyst at T=300°C Base catalyst weight = 0.5 g, ZSM-5 weight = 0 g, H ₂ /CO ratio = 1, total feed rate = 100 scc/min, reactor pressure = 300 psi, TOS = 24-48 h, Organic phase wt = 5.6 g, Aqueous phase wt = 2.41 g							
Aromatics	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
toluene	0	0	7	92	0	0	0
p-xylene	0	0	8	106	0	0	0
propyl-benzene	0	0	9	120	0	0	0
butyl-benzene	0	0	10	134	0	0	0
		0					
n-praffins	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
n-C ₅	0.5997	0.0336	5	44	0.0008	0.0005	0.0458
n-C ₆	5.0062	0.2803	6	86	0.0033	0.0023	0.2347
n-C ₇	5.6074	0.3140	7	100	0.0031	0.0022	0.2638
n-C ₈	7.0865	0.3968	8	114	0.0035	0.0024	0.3342
n-C ₉	5.3976	0.3023	9	128	0.0024	0.0016	0.2550
n-C ₁₀	3.7127	0.2079	10	142	0.0015	0.0010	0.1757
n-C ₁₁	2.7239	0.1525	11	156	0.0010	0.0007	0.1291
n-C ₁₂	1.9904	0.1115	12	170	0.0007	0.0005	0.0944
n-C ₁₃	1.4874	0.0833	13	184	0.0005	0.0003	0.0706
n-C ₁₄	1.1287	0.0632	14	198	0.0003	0.0002	0.0536
n-C ₁₅	0.8212	0.0460	15	212	0.0002	0.0002	0.0390
n-C ₁₆	0.7018	0.0393	16	226	0.0002	0.0001	0.0334
n-C ₁₇₊	2.5458	0.1426	17	240	0.0006	0.0004	0.1212
i-paraffins	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
i-C ₅	7.9348	0.4443	5	44	0.0101	0.0070	0.6059
i-C ₆	4.1100	0.2302	6	86	0.0027	0.0019	0.1927
i-C ₇	11.4422	0.6408	7	100	0.0064	0.0044	0.5382
i-C ₈	12.8977	0.7223	8	114	0.0063	0.0044	0.6082
i-C ₉	7.1375	0.3997	9	128	0.0031	0.0022	0.3372
i-C ₁₀	4.7582	0.2665	10	142	0.0019	0.0013	0.2252
i-C ₁₁	3.1895	0.1786	11	156	0.0011	0.0008	0.1511
i-C ₁₂	2.1156	0.1185	12	170	0.0007	0.0005	0.1004
i-C ₁₃	1.4761	0.0827	13	184	0.0004	0.0003	0.0701
i-C ₁₄	1.0062	0.0563	14	198	0.0003	0.0002	0.0478
i-C ₁₅	1.1970	0.0670	15	212	0.0003	0.0002	0.0569
i-C ₁₆	0.5966	0.0334	16	226	0.0001	0.0001	0.0284
i-C ₁₇₊	3.1790	0.1780	17	240	0.0007	0.0005	0.1513
						Total in oil	4.9641
Alcohols	wt % in aqueous liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
Methanol	10.1000	0.2434	1	32	0.0076	0.0053	0.0913
Ethanol	21.3948	0.5156	2	46	0.0112	0.0078	0.2690
2-Propanol	3.8000	0.0916	3	60	0.0015	0.0011	0.0549
1-Propanol	11.3000	0.2723	3	60	0.0045	0.0032	0.1634
2-Butanol	1.3000	0.0313	4	74	0.0004	0.0003	0.0203
1-Butanol	8.5000	0.2049	4	74	0.0028	0.0019	0.1329
2-Pentanol	0.0000	0.0000	5	88	0.0000	0.0000	0.0000
1-Pentanol	6.5000	0.1567	5	88	0.0018	0.0012	0.1068
Water	37.1000	0.8941	0	18	0.0497	0.0345	0.0000
						Total in aqueous	0.7474
Total carbon due to oil and aqueous phase			5.7114 g carbon /day				

Base case catalyst at T=320°C Base catalyst weight = 0.5 g, ZSM-5 weight = 0 g, H ₂ /CO ratio = 1, total feed rate = 100 scc/min, reactor pressure = 300 psi, TOS = 24-48 h, Organic phase wt = 4.8 g, Aqueous phase wt = 3.2 g							
Aromatics	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
toluene	0.0000	0.0000	7	92	0.0000	0.0000	0.0000
p-xylene	0.0000	0.0000	8	106	0.0000	0.0000	0.0000
propyl-benzene	0.0000	0.0000	9	120	0.0000	0.0000	0.0000
butyl-benzene	0.0000	0.0000	10	134	0.0000	0.0000	0.0000
n-praffins	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
n-C ₅	0.1048	0.0050	5	44	0.0001	0.0001	0.0069
n-C ₆	1.2406	0.0595	6	86	0.0007	0.0005	0.0499
n-C ₇	2.2444	0.1077	7	100	0.0011	0.0007	0.0905
n-C ₈	3.0958	0.1486	8	114	0.0013	0.0009	0.1251
n-C ₉	2.8261	0.1357	9	128	0.0011	0.0007	0.1145
n-C ₁₀	2.3262	0.1117	10	142	0.0008	0.0005	0.0944
n-C ₁₁	2.0307	0.0975	11	156	0.0006	0.0004	0.0825
n-C ₁₂	1.8018	0.0865	12	170	0.0005	0.0004	0.0733
n-C ₁₃	1.6289	0.0782	13	184	0.0004	0.0003	0.0663
n-C ₁₄	1.4888	0.0715	14	198	0.0004	0.0003	0.0606
n-C ₁₅	1.3495	0.0648	15	212	0.0003	0.0002	0.0550
n-C ₁₆	1.2316	0.0591	16	226	0.0003	0.0002	0.0502
n-C ₁₇₊	7.0452	0.3382	17	240	0.0014	0.0010	0.2874
i-paraffins	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
i-C ₅	2.2486	0.1079	5	44	0.0025	0.0017	0.1472
i-C ₆	4.1912	0.2012	6	86	0.0023	0.0016	0.1684
i-C ₇	10.1042	0.4850	7	100	0.0049	0.0034	0.4074
i-C ₈	11.4157	0.5480	8	114	0.0048	0.0033	0.4614
i-C ₉	9.2423	0.4436	9	128	0.0035	0.0024	0.3743
i-C ₁₀	7.4218	0.3562	10	142	0.0025	0.0017	0.3011
i-C ₁₁	5.9118	0.2838	11	156	0.0018	0.0013	0.2401
i-C ₁₂	4.5354	0.2177	12	170	0.0013	0.0009	0.1844
i-C ₁₃	3.5116	0.1686	13	184	0.0009	0.0006	0.1429
i-C ₁₄	2.7191	0.1305	14	198	0.0007	0.0005	0.1107
i-C ₁₅	2.1167	0.1016	15	212	0.0005	0.0003	0.0863
i-C ₁₆	1.6376	0.0786	16	226	0.0003	0.0002	0.0668
i-C ₁₇₊	6.5297	0.3134	17	240	0.0013	0.0009	0.2664
						Total in oil	4.1139
Alcohols	wt % in aqueous liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
Methanol	9.6000	0.3072	1	32	0.0096	0.0067	0.1152
Ethanol	18.6000	0.5952	2	46	0.0129	0.0090	0.3105
2-Propanol	3.6000	0.1152	3	60	0.0019	0.0013	0.0691
1-Propanol	8.6000	0.2752	3	60	0.0046	0.0032	0.1651
2-Butanol	0.8000	0.0256	4	74	0.0003	0.0002	0.0166
1-Butanol	4.2000	0.1344	4	74	0.0018	0.0013	0.0872
2-Pentanol	0.0000	0.0000	5	88	0.0000	0.0000	0.0000
1-Pentanol	2.6000	0.0832	5	88	0.0009	0.0007	0.0567
Water	52.0000	1.6640	0	18	0.0924	0.0642	0.0000
						Total in aqueous	0.7053
Total carbon due to oil and aqueous phase			4.8192 g carbon /day				

Separate-bed catalyst arrangement, ZSM-5 weight = 0.25 g Base catalyst weight = 0.5 g, T=300°C, H ₂ /CO ratio = 1, total feed rate = 100 scc/min, reactor pressure = 300 psi, TOS = 24-48 h, Organic phase wt = 7.2902 g, Aqueous phase wt = 2.4 g							
Aromatics	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
Toluene	1.3638	0.0994	7	92	0.0011	0.0008	0.0908
p-xylene	2.3034	0.1679	8	106	0.0016	0.0011	0.1521
propyl-benzene	2.1294	0.1552	9	120	0.0013	0.0009	0.1397
butyl-benzene	0.6555	0.0478	10	134	0.0004	0.0002	0.0428
n-praffins	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
n-C ₅	0.7134	0.0520	5	44	0.0012	0.0008	0.0709
n-C ₆	5.2186	0.3804	6	86	0.0044	0.0031	0.3185
n-C ₇	8.7701	0.6394	7	100	0.0064	0.0044	0.5371
n-C ₈	4.1738	0.3043	8	114	0.0027	0.0019	0.2562
n-C ₉	2.6472	0.1930	9	128	0.0015	0.0010	0.1628
n-C ₁₀	2.1503	0.1568	10	142	0.0011	0.0008	0.1325
n-C ₁₁	1.2047	0.0878	11	156	0.0006	0.0004	0.0743
n-C ₁₂	0.5045	0.0368	12	170	0.0002	0.0002	0.0312
n-C ₁₃	0.3033	0.0221	13	184	0.0001	0.0001	0.0187
n-C ₁₄	0.2147	0.0157	14	198	0.0001	0.0001	0.0133
n-C ₁₅	0.0907	0.0066	15	212	0.0000	0.0000	0.0056
n-C ₁₆	0.0143	0.0010	16	226	0.0000	0.0000	0.0009
n-C ₁₇₊	0.0490	0.0036	17	240	0.0000	0.0000	0.0030
i-paraffins	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
i-C ₅	2.9301	0.2136	5	44	0.0049	0.0034	0.2913
i-C ₆	2.3980	0.1748	6	86	0.0020	0.0014	0.1464
i-C ₇	24.8467	1.8114	7	100	0.0181	0.0126	1.5216
i-C ₈	17.8412	1.3007	8	114	0.0114	0.0079	1.0953
i-C ₉	7.8106	0.5694	9	128	0.0044	0.0031	0.4804
i-C ₁₀	5.6662	0.4131	10	142	0.0029	0.0020	0.3491
i-C ₁₁	2.8323	0.2065	11	156	0.0013	0.0009	0.1747
i-C ₁₂	1.5930	0.1161	12	170	0.0007	0.0005	0.0984
i-C ₁₃	0.5345	0.0390	13	184	0.0002	0.0001	0.0330
i-C ₁₄	0.4944	0.0360	14	198	0.0002	0.0001	0.0306
i-C ₁₅	0.1682	0.0123	15	212	0.0001	0.0000	0.0104
i-C ₁₆	0.2408	0.0176	16	226	0.0001	0.0001	0.0149
i-C ₁₇₊	0.1374	0.0100	17	240	0.0000	0.0000	0.0085
						Total in oil	6.3050
Alcohols	wt % in aqueous liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
Methanol	0.0047	0.0001	1	32	0.0000	0.0000	0.0000
Ethanol	0.0011	0.0000	2	46	0.0000	0.0000	0.0000
2-Propanol	4.3418	0.1042	3	60	0.0017	0.0012	0.0625
1-Propanol	0.0000	0.0000	3	60	0.0000	0.0000	0.0000
2-Butanol	0.5820	0.0140	4	74	0.0002	0.0001	0.0091
1-Butanol	0.0000	0.0000	4	74	0.0000	0.0000	0.0000
2-Pentanol	0.0083	0.0002	5	88	0.0000	0.0000	0.0001
1-Pentanol	0.0000	0.0000	5	88	0.0000	0.0000	0.0000
water	95.0621	2.2815	0	18	0.1267	0.0880	0.0000
						Total in aqueous	0.0717
Total carbon due to oil and aqueous phase			6.3767 g carbon /day				

Separate-bed catalyst arrangement, ZSM-5 weight = 0.5 g Base catalyst weight = 0.5 g, T=300°C, H ₂ /CO ratio = 1, total feed rate = 100 scc/min, reactor pressure = 300 psi, TOS = 24-48 h, Organic phase wt = 7.3875 g, Aqueous phase wt = 2.3 g							
Aromatics	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
toluene	6.8455	0.5057	7	92	0.0055	0.0038	0.4617
p-xylene	11.0089	0.8133	8	106	0.0077	0.0053	0.7366
propyl-benzene	8.4654	0.6254	9	120	0.0052	0.0036	0.5628
butyl-benzene	1.3622	0.1006	10	134	0.0008	0.0005	0.0901
n-praffins	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
n-C ₅	1.0289	0.0760	5	44	0.0017	0.0012	0.1036
n-C ₆	4.3825	0.3238	6	86	0.0038	0.0026	0.2711
n-C ₇	2.7556	0.2036	7	100	0.0020	0.0014	0.1710
n-C ₈	1.1798	0.0872	8	114	0.0008	0.0005	0.0734
n-C ₉	0.9667	0.0714	9	128	0.0006	0.0004	0.0603
n-C ₁₀	0.8891	0.0657	10	142	0.0005	0.0003	0.0555
n-C ₁₁	0.4850	0.0358	11	156	0.0002	0.0002	0.0303
n-C ₁₂	0.3497	0.0258	12	170	0.0002	0.0001	0.0219
n-C ₁₃	0.2169	0.0160	13	184	0.0001	0.0001	0.0136
n-C ₁₄	0.3071	0.0227	14	198	0.0001	0.0001	0.0193
n-C ₁₅	0.0596	0.0044	15	212	0.0000	0.0000	0.0037
n-C ₁₆	0.0373	0.0028	16	226	0.0000	0.0000	0.0023
n-C ₁₇₊	0.2703	0.0200	17	240	0.0001	0.0001	0.0170
i-paraffins	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
i-C ₅	1.2832	0.0948	5	44	0.0022	0.0015	0.1293
i-C ₆	2.4117	0.1782	6	86	0.0021	0.0014	0.1492
i-C ₇	13.9700	1.0320	7	100	0.0103	0.0072	0.8669
i-C ₈	12.9020	0.9531	8	114	0.0084	0.0058	0.8026
i-C ₉	8.4753	0.6261	9	128	0.0049	0.0034	0.5283
i-C ₁₀	7.8914	0.5830	10	142	0.0041	0.0029	0.4927
i-C ₁₁	3.7504	0.2771	11	156	0.0018	0.0012	0.2344
i-C ₁₂	4.4465	0.3285	12	170	0.0019	0.0013	0.2782
i-C ₁₃	2.2063	0.1630	13	184	0.0009	0.0006	0.1382
i-C ₁₄	1.3136	0.0970	14	198	0.0005	0.0003	0.0823
i-C ₁₅	0.3917	0.0289	15	212	0.0001	0.0001	0.0246
i-C ₁₆	0.1660	0.0123	16	226	0.0001	0.0000	0.0104
i-C ₁₇₊	0.2266	0.0167	17	240	0.0001	0.0000	0.0142
						Sum in oil	6.4456
Alcohols	wt % in aqueous liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
Methanol	0.0000	0.0000	1	32	0.0000	0.0000	0.0000
Ethanol	0.0558	0.0012	2	46	0.0000	0.0000	0.0006
2-Propanol	0.1807	0.0038	3	60	0.0001	0.0000	0.0023
1-Propanol	0.0000	0.0000	3	60	0.0000	0.0000	0.0000
2-Butanol	0.0000	0.0000	4	74	0.0000	0.0000	0.0000
1-Butanol	0.0000	0.0000	4	74	0.0000	0.0000	0.0000
2-Pentanol	0.0000	0.0000	5	88	0.0000	0.0000	0.0000
1-Pentanol	0.0000	0.0000	5	88	0.0000	0.0000	0.0000
Water	99.7634	2.1075	0	18	0.1171	0.0813	0.0000
						Total in aqueous	0.0029
Total carbon due to oil and aqueous phase			6.4485 g carbon /day				

Separate-bed catalyst arrangement, ZSM-5 weight = 1 g Base catalyst weight = 0.5 g, T=300°C, H ₂ /CO ratio = 1, total feed rate = 100 scc/min, reactor pressure = 300 psi, TOS = 24-48 h, Organic phase wt = 5.6756 g, Aqueous phase wt = 2.5 g							
Aromatics	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
toluene	15.2457	0.8653	7	92	0.0094	0.0065	0.7900
p-xylene	16.5359	0.9385	8	106	0.0089	0.0061	0.8500
propyl-benzene	10.0745	0.5718	9	120	0.0048	0.0033	0.5146
butyl-benzene	1.0935	0.0621	10	134	0.0005	0.0003	0.0556
n-praffins	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
n-C ₅	1.6643	0.0945	5	44	0.0021	0.0015	0.1288
n-C ₆	1.6399	0.0931	6	86	0.0011	0.0008	0.0779
n-C ₇	0.4166	0.0236	7	100	0.0002	0.0002	0.0199
n-C ₈	0.0769	0.0044	8	114	0.0000	0.0000	0.0037
n-C ₉	0.0634	0.0036	9	128	0.0000	0.0000	0.0030
n-C ₁₀	0.0740	0.0042	10	142	0.0000	0.0000	0.0036
n-C ₁₁	0.4098	0.0233	11	156	0.0001	0.0001	0.0197
n-C ₁₂	0.1071	0.0061	12	170	0.0000	0.0000	0.0051
n-C ₁₃	0.1052	0.0060	13	184	0.0000	0.0000	0.0051
n-C ₁₄	0.3754	0.0213	14	198	0.0001	0.0001	0.0181
n-C ₁₅	0.0591	0.0034	15	212	0.0000	0.0000	0.0028
n-C ₁₆	0.0565	0.0032	16	226	0.0000	0.0000	0.0027
n-C ₁₇₊	0.0326	0.0018	17	240	0.0000	0.0000	0.0016
i-paraffins	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
i-C ₅	6.5901	0.3740	5	44	0.0085	0.0059	0.5100
i-C ₆	3.6867	0.2092	6	86	0.0024	0.0017	0.1752
i-C ₇	10.5824	0.6006	7	100	0.0060	0.0042	0.5045
i-C ₈	6.3608	0.3610	8	114	0.0032	0.0022	0.3040
i-C ₉	5.3770	0.3052	9	128	0.0024	0.0017	0.2575
i-C ₁₀	7.3999	0.4200	10	142	0.0030	0.0021	0.3549
i-C ₁₁	3.3578	0.1906	11	156	0.0012	0.0008	0.1613
i-C ₁₂	3.2602	0.1850	12	170	0.0011	0.0008	0.1567
i-C ₁₃	2.1474	0.1219	13	184	0.0007	0.0005	0.1033
i-C ₁₄	1.7614	0.1000	14	198	0.0005	0.0004	0.0848
i-C ₁₅	0.8845	0.0502	15	212	0.0002	0.0002	0.0426
i-C ₁₆	0.3872	0.0220	16	226	0.0001	0.0001	0.0187
i-C ₁₇₊	0.1711	0.0097	17	240	0.0000	0.0000	0.0083
						Total in oil	5.1840
Alcohols	wt % in aqueous liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
Methanol	0.0000	0.0000	1	32	0.0000	0.0000	0.0000
Ethanol	0.0000	0.0000	2	46	0.0000	0.0000	0.0000
2-Propanol	0.1000	0.0021	3	60	0.0000	0.0000	0.0013
1-Propanol	0.0000	0.0000	3	60	0.0000	0.0000	0.0000
2-Butanol	0.2000	0.0042	4	74	0.0001	0.0000	0.0027
1-Butanol	0.0000	0.0000	4	74	0.0000	0.0000	0.0000
2-Pentanol	0.0000	0.0000	5	88	0.0000	0.0000	0.0000
1-Pentanol	0.0000	0.0000	5	88	0.0000	0.0000	0.0000
Water	99.7000	2.1062	0	18	0.1170	0.0813	0.0000
						Total in aqueous	0.0040
Total carbon due to oil and aqueous phase			5.1880 g carbon /day				

Separate-bed catalyst arrangement, T=280°C Base catalyst weight = 0.5 g, ZSM-5 weight = 0.5 g, H ₂ /CO ratio = 1, total feed rate = 100 scc/min, reactor pressure = 300 psi, TOS = 24-48 h, Organic phase wt = 3.25 g, Aqueous phase wt = 1.5 g							
Aromatics	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
toluene	1.0357	0.0337	7.0000	92.0000	0.0004	0.0003	0.0307
p-xylene	3.3722	0.1096	8.0000	106.0000	0.0010	0.0007	0.0993
propyl-benzene	3.3797	0.1098	9.0000	120.0000	0.0009	0.0006	0.0989
butyl-benzene	1.1367	0.0369	10.0000	134.0000	0.0003	0.0002	0.0331
n-praffins	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
n-C ₅	0.6063	0.0197	5	44	0.0004	0.0003	0.0269
n-C ₆	5.6893	0.1849	6	86	0.0022	0.0015	0.1548
n-C ₇	5.0600	0.1645	7	100	0.0016	0.0011	0.1381
n-C ₈	3.1135	0.1012	8	114	0.0009	0.0006	0.0852
n-C ₉	2.5818	0.0839	9	128	0.0007	0.0005	0.0708
n-C ₁₀	2.0503	0.0666	10	142	0.0005	0.0003	0.0563
n-C ₁₁	0.5547	0.0180	11	156	0.0001	0.0001	0.0153
n-C ₁₂	0.3289	0.0107	12	170	0.0001	0.0000	0.0091
n-C ₁₃	0.1538	0.0050	13	184	0.0000	0.0000	0.0042
n-C ₁₄	0.1524	0.0050	14	198	0.0000	0.0000	0.0042
n-C ₁₅	0.1205	0.0039	15	212	0.0000	0.0000	0.0033
n-C ₁₆	0.0989	0.0032	16	226	0.0000	0.0000	0.0027
n-C ₁₇₊	0.1569	0.0051	17	240	0.0000	0.0000	0.0043
i-paraffins	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
i-C ₅	2.2777	0.0740	5	44	0.0017	0.0012	0.1009
i-C ₆	1.8112	0.0589	6	86	0.0007	0.0005	0.0493
i-C ₇	16.8435	0.5474	7	100	0.0055	0.0038	0.4598
i-C ₈	18.5675	0.6034	8	114	0.0053	0.0037	0.5082
i-C ₉	12.3717	0.4021	9	128	0.0031	0.0022	0.3393
i-C ₁₀	8.6809	0.2821	10	142	0.0020	0.0014	0.2384
i-C ₁₁	4.9417	0.1606	11	156	0.0010	0.0007	0.1359
i-C ₁₂	2.8981	0.0942	12	170	0.0006	0.0004	0.0798
i-C ₁₃	0.8350	0.0271	13	184	0.0001	0.0001	0.0230
i-C ₁₄	0.4625	0.0150	14	198	0.0001	0.0001	0.0128
i-C ₁₅	0.2233	0.0073	15	212	0.0000	0.0000	0.0062
i-C ₁₆	0.0408	0.0013	16	226	0.0000	0.0000	0.0011
i-C ₁₇₊	0.4539	0.0148	17	240	0.0001	0.0000	0.0125
						Total in oil	2.8044
Alcohols	wt % in aqueous liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
Methanol	0.1000	0.0015	1	32	0.0000	0.0000	0.0006
Ethanol	0.3000	0.0045	2	46	0.0001	0.0001	0.0023
2-Propanol	2.3100	0.0347	3	60	0.0006	0.0004	0.0208
1-Propanol	0.0000	0.0000	3	60	0.0000	0.0000	0.0000
2-Butanol	0.1000	0.0015	4	74	0.0000	0.0000	0.0010
1-Butanol	0.0000	0.0000	4	74	0.0000	0.0000	0.0000
2-Pentanol	0.0000	0.0000	5	88	0.0000	0.0000	0.0000
1-Pentanol	0.0000	0.0000	5	88	0.0000	0.0000	0.0000
Water	97.1900	1.4579	0	18	0.0810	0.0562	0.0000
						Total in aqueous	0.0241
Total carbon due to oil and aqueous phase			2.8285 g carbon /day				

Separate-bed catalyst arrangement, T=320°C							
Base catalyst weight = 0.5 g, ZSM-5 weight = 0.5 g, H ₂ /CO ratio = 1,							
total feed rate = 100 scc/min, reactor pressure = 300 psi, TOS = 24-48 h, Organic phase wt = 57802 g, Aqueous phase wt = 1.5 g							
Aromatics	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
toluene	3.0615	0.1770	7	92	0.0019	0.0013	0.1616
p-xylene	7.0070	0.4050	8	106	0.0038	0.0027	0.3668
propyl-benzene	5.8745	0.3396	9	120	0.0028	0.0020	0.3056
butyl-benzene	1.3564	0.0784	10	134	0.0006	0.0004	0.0702
n-praffins	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
n-C ₅	1.0999	0.0636	5	44	0.0014	0.0010	0.0867
n-C ₆	4.2079	0.2432	6	86	0.0028	0.0020	0.2036
n-C ₇	3.5942	0.2077	7	100	0.0021	0.0014	0.1745
n-C ₈	1.3840	0.0800	8	114	0.0007	0.0005	0.0674
n-C ₉	0.7068	0.0409	9	128	0.0003	0.0002	0.0345
n-C ₁₀	1.1379	0.0658	10	142	0.0005	0.0003	0.0556
n-C ₁₁	0.7025	0.0406	11	156	0.0003	0.0002	0.0344
n-C ₁₂	0.2084	0.0120	12	170	0.0001	0.0000	0.0102
n-C ₁₃	0.1339	0.0077	13	184	0.0000	0.0000	0.0066
n-C ₁₄	0.1047	0.0060	14	198	0.0000	0.0000	0.0051
n-C ₁₅	0.0448	0.0026	15	212	0.0000	0.0000	0.0022
n-C ₁₆	0.0432	0.0025	16	226	0.0000	0.0000	0.0021
n-C ₁₇₊	0.0234	0.0014	17	240	0.0000	0.0000	0.0012
i-paraffins	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
i-C ₅	1.0999	0.0636	5	44	0.0014	0.0010	0.0867
i-C ₆	4.2079	0.2432	6	86	0.0028	0.0020	0.2036
i-C ₇	3.5942	0.2077	7	100	0.0021	0.0014	0.1745
i-C ₈	1.3840	0.0800	8	114	0.0007	0.0005	0.0674
i-C ₉	0.7068	0.0409	9	128	0.0003	0.0002	0.0345
i-C ₁₀	1.1379	0.0658	10	142	0.0005	0.0003	0.0556
i-C ₁₁	0.7025	0.0406	11	156	0.0003	0.0002	0.0344
i-C ₁₂	0.2084	0.0120	12	170	0.0001	0.0000	0.0102
i-C ₁₃	0.1339	0.0077	13	184	0.0000	0.0000	0.0066
i-C ₁₄	0.1047	0.0060	14	198	0.0000	0.0000	0.0051
i-C ₁₅	0.0448	0.0026	15	212	0.0000	0.0000	0.0022
i-C ₁₆	0.0432	0.0025	16	226	0.0000	0.0000	0.0021
i-C ₁₇₊	0.0234	0.0014	17	240	0.0000	0.0000	0.0012
						Total in oil	2.2722
Alcohols	wt % in aqueous liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
Methanol	0.0000	0.0000	1	32	0.0000	0.0000	0.0000
Ethanol	0.0000	0.0000	2	46	0.0000	0.0000	0.0000
2-Propanol	0.3000	0.0045	3	60	0.0001	0.0001	0.0027
1-Propanol	0.0000	0.0000	3	60	0.0000	0.0000	0.0000
2-Butanol	0.0000	0.0000	4	74	0.0000	0.0000	0.0000
1-Butanol	0.0000	0.0000	4	74	0.0000	0.0000	0.0000
2-Pentanol	0.0000	0.0000	5	88	0.0000	0.0000	0.0000
1-Pentanol	0.0000	0.0000	5	88	0.0000	0.0000	0.0000
water	99.7000	1.4955	0	18	0.0831	0.0577	0.0000
						Total in aqueous	0.0027
Total carbon due to oil and aqueous phase			2.2749 g carbon /day				

Mixed-bed catalyst arrangement, ZSM-5 weight = 0.25 g Base catalyst weight = 0.5 g, T=300°C, H ₂ /CO ratio = 1, total feed rate = 100 scc/min, reactor pressure = 300 psi, TOS = 24-48 h, Organic phase wt = 3.7476 g, Aqueous phase wt = 1.2 g							
Aromatics	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
toluene	2.0917	0.0784	7	92	0.0009	0.0006	0.0716
p-xylene	5.0754	0.1902	8	106	0.0018	0.0012	0.1723
propyl-benzene	4.7711	0.1788	9	120	0.0015	0.0010	0.1609
butyl-benzene	0.9424	0.0353	10	134	0.0003	0.0002	0.0316
n-praffins	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
n-C ₅	0.1960	0.0073	5	44	0.0002	0.0001	0.0100
n-C ₆	5.8053	0.2176	6	86	0.0025	0.0018	0.1821
n-C ₇	6.3243	0.2370	7	100	0.0024	0.0016	0.1991
n-C ₈	3.3020	0.1237	8	114	0.0011	0.0008	0.1042
n-C ₉	2.3884	0.0895	9	128	0.0007	0.0005	0.0755
n-C ₁₀	1.7604	0.0660	10	142	0.0005	0.0003	0.0558
n-C ₁₁	0.1776	0.0067	11	156	0.0000	0.0000	0.0056
n-C ₁₂	0.6218	0.0233	12	170	0.0001	0.0001	0.0197
n-C ₁₃	0.4922	0.0184	13	184	0.0001	0.0001	0.0156
n-C ₁₄	0.0432	0.0016	14	198	0.0000	0.0000	0.0014
n-C ₁₅	0.3099	0.0116	15	212	0.0001	0.0000	0.0099
n-C ₁₆	0.2626	0.0098	16	226	0.0000	0.0000	0.0084
n-C ₁₇₊	0.4130	0.0155	17	240	0.0001	0.0000	0.0132
i-paraffins	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
i-C ₅	2.8035	0.1051	5	44	0.0024	0.0017	0.1433
i-C ₆	2.9994	0.1124	6	86	0.0013	0.0009	0.0941
i-C ₇	17.0442	0.6387	7	100	0.0064	0.0044	0.5365
i-C ₈	15.4824	0.5802	8	114	0.0051	0.0035	0.4886
i-C ₉	9.6031	0.3599	9	128	0.0028	0.0020	0.3037
i-C ₁₀	7.8008	0.2923	10	142	0.0021	0.0014	0.2471
i-C ₁₁	4.8371	0.1813	11	156	0.0012	0.0008	0.1534
i-C ₁₂	2.2294	0.0836	12	170	0.0005	0.0003	0.0708
i-C ₁₃	0.7713	0.0289	13	184	0.0002	0.0001	0.0245
i-C ₁₄	0.7620	0.0286	14	198	0.0001	0.0001	0.0242
i-C ₁₅	0.1863	0.0070	15	212	0.0000	0.0000	0.0059
i-C ₁₆	0.1774	0.0066	16	226	0.0000	0.0000	0.0056
i-C ₁₇₊	0.3256	0.0122	17	240	0.0001	0.0000	0.0104
						Total in oil	3.2450
Alcohols	wt % in aqueous liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
Methanol	10.5000	0.1260	1	32	0.0039	0.0027	0.0473
Ethanol	20.6000	0.2472	2	46	0.0054	0.0037	0.1290
2-Propanol	4.2000	0.0504	3	60	0.0008	0.0006	0.0302
1-Propanol	9.8000	0.1176	3	60	0.0020	0.0014	0.0706
2-Butanol	1.4000	0.0168	4	74	0.0002	0.0002	0.0109
1-Butanol	7.8000	0.0936	4	74	0.0013	0.0009	0.0607
2-Pentanol	0.0000	0.0000	5	88	0.0000	0.0000	0.0000
1-Pentanol	6.4000	0.0768	5	88	0.0009	0.0006	0.0524
Water	39.3000	0.4716	0	18	0.0262	0.0182	0.0000
						Total in aqueous	0.3537
Total carbon due to oil and aqueous phase			3.5987 g carbon /day				

Mixed-bed catalyst arrangement, ZSM-5 weight = 0.5 g Base catalyst weight = 0.5 g, T=300°C, H ₂ /CO ratio = 1, total feed rate = 100 scc/min, reactor pressure = 300 psi, TOS = 24-48 h, Organic phase wt = 4.2094g, Aqueous phase wt = 1.5 g							
Aromatics	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
toluene	3.8369	0.1615	7	92	0.0018	0.0012	0.1475
p-xylene	9.3795	0.3948	8	106	0.0037	0.0026	0.3576
propyl-benzene	7.7203	0.3250	9	120	0.0027	0.0019	0.2925
butyl-benzene	1.2106	0.0510	10	134	0.0004	0.0003	0.0456
		0.0000					
n-praffins	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
n-C ₅	0.7774	0.0327	5	44	0.0007	0.0005	0.0446
n-C ₆	3.8665	0.1628	6	86	0.0019	0.0013	0.1363
n-C ₇	3.8877	0.1637	7	100	0.0016	0.0011	0.1375
n-C ₈	1.9161	0.0807	8	114	0.0007	0.0005	0.0679
n-C ₉	1.5164	0.0638	9	128	0.0005	0.0003	0.0539
n-C ₁₀	1.1022	0.0464	10	142	0.0003	0.0002	0.0392
n-C ₁₁	0.1297	0.0055	11	156	0.0000	0.0000	0.0046
n-C ₁₂	0.5038	0.0212	12	170	0.0001	0.0001	0.0180
n-C ₁₃	0.5127	0.0216	13	184	0.0001	0.0001	0.0183
n-C ₁₄	0.4908	0.0207	14	198	0.0001	0.0001	0.0175
n-C ₁₅	0.3016	0.0127	15	212	0.0001	0.0000	0.0108
n-C ₁₆	0.2824	0.0119	16	226	0.0001	0.0000	0.0101
n-C ₁₇₊	1.0857	0.0457	17	240	0.0002	0.0001	0.0388
i-paraffins	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
i-C ₅	2.3723	0.0999	5	44	0.0023	0.0016	0.1362
i-C ₆	2.7912	0.1175	6	86	0.0014	0.0009	0.0984
i-C ₇	15.4657	0.6510	7	100	0.0065	0.0045	0.5469
i-C ₈	14.2032	0.5979	8	114	0.0052	0.0036	0.5035
i-C ₉	8.1685	0.3438	9	128	0.0027	0.0019	0.2901
i-C ₁₀	8.2233	0.3462	10	142	0.0024	0.0017	0.2925
i-C ₁₁	4.3375	0.1826	11	156	0.0012	0.0008	0.1545
i-C ₁₂	2.4700	0.1040	12	170	0.0006	0.0004	0.0881
i-C ₁₃	1.3396	0.0564	13	184	0.0003	0.0002	0.0478
i-C ₁₄	0.9463	0.0398	14	198	0.0002	0.0001	0.0338
i-C ₁₅	0.3459	0.0146	15	212	0.0001	0.0000	0.0124
i-C ₁₆	0.3103	0.0131	16	226	0.0001	0.0000	0.0111
i-C ₁₇₊	0.5055	0.0213	17	240	0.0001	0.0001	0.0181
						Total in oil	3.6739
Alcohols	wt % in aqueous liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
Methanol	8.5000	0.1275	1	32	0.0040	0.0028	0.0478
Ethanol	18.2000	0.2730	2	46	0.0059	0.0041	0.1424
2-Propanol	2.9000	0.0435	3	60	0.0007	0.0005	0.0261
1-Propanol	6.8000	0.1020	3	60	0.0017	0.0012	0.0612
2-Butanol	1.1000	0.0165	4	74	0.0002	0.0002	0.0107
1-Butanol	6.2000	0.0930	4	74	0.0013	0.0009	0.0603
2-Pentanol	0.0000	0.0000	5	88	0.0000	0.0000	0.0000
1-Pentanol	2.1000	0.0315	5	88	0.0004	0.0002	0.0215
Water	54.2000	0.8130	0	18	0.0452	0.0314	0.0000
						Total in aqueous	0.3222
Total carbon due to oil and aqueous phase			3.9961 g carbon /day				

Mixed-bed catalyst arrangement, ZSM-5 weight = 1 g Base catalyst weight = 0.5 g, T=300°C, H ₂ /CO ratio = 1, total feed rate = 100 scc/min, reactor pressure = 300 Psi, TOS = 24-48 h, Organic phase wt = 3.0891 g, Aqueous phase wt = 2.3 g							
Aromatics	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
toluene	4.9485	0.1529	7	92	0.0017	0.0012	0.1396
p-xylene	10.5501	0.3259	8	106	0.0031	0.0021	0.2952
propyl-benzene	8.4248	0.2603	9	120	0.0022	0.0015	0.2342
butyl-benzene	1.1905	0.0368	10	134	0.0003	0.0002	0.0329
		0.0000					
n-praffins	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
n-C ₅	1.4829	0.0458	5	44	0.0010	0.0007	0.0625
n-C ₆	4.6485	0.1436	6	86	0.0017	0.0012	0.1202
n-C ₇	3.8531	0.1190	7	100	0.0012	0.0008	0.1000
n-C ₈	1.6444	0.0508	8	114	0.0004	0.0003	0.0428
n-C ₉	1.0613	0.0328	9	128	0.0003	0.0002	0.0277
n-C ₁₀	0.7200	0.0222	10	142	0.0002	0.0001	0.0188
n-C ₁₁	0.4823	0.0149	11	156	0.0001	0.0001	0.0126
n-C ₁₂	0.2281	0.0070	12	170	0.0000	0.0000	0.0060
n-C ₁₃	0.3053	0.0094	13	184	0.0001	0.0000	0.0080
n-C ₁₄	0.2624	0.0081	14	198	0.0000	0.0000	0.0069
n-C ₁₅	0.0000	0.0000	15	212	0.0000	0.0000	0.0000
n-C ₁₆	0.0000	0.0000	16	226	0.0000	0.0000	0.0000
n-C ₁₇₊	0.0000	0.0000	17	240	0.0000	0.0000	0.0000
i-paraffins	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
i-C ₅	4.1856	0.1293	5	44	0.0029	0.0020	0.1763
i-C ₆	3.0916	0.0955	6	86	0.0011	0.0008	0.0800
i-C ₇	16.5978	0.5127	7	100	0.0051	0.0036	0.4307
i-C ₈	12.6468	0.3907	8	114	0.0034	0.0024	0.3290
i-C ₉	5.0421	0.1558	9	128	0.0012	0.0008	0.1314
i-C ₁₀	6.4920	0.2005	10	142	0.0014	0.0010	0.1695
i-C ₁₁	3.7736	0.1166	11	156	0.0007	0.0005	0.0986
i-C ₁₂	2.5339	0.0783	12	170	0.0005	0.0003	0.0663
i-C ₁₃	0.7627	0.0236	13	184	0.0001	0.0001	0.0200
i-C ₁₄	0.7509	0.0232	14	198	0.0001	0.0001	0.0197
i-C ₁₅	0.4616	0.0143	15	212	0.0001	0.0000	0.0121
i-C ₁₆	0.0000	0.0000	16	226	0.0000	0.0000	0.0000
i-C ₁₇₊	0.0000	0.0000	17	240	0.0000	0.0000	0.0000
						Total in oil	2.6408
Alcohols	wt % in aqueous liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
Methanol	2.8000	0.0644	1	32	0.0020	0.0014	0.0242
Ethanol	4.1000	0.0943	2	46	0.0021	0.0014	0.0492
2-Propanol	1.1000	0.0253	3	60	0.0004	0.0003	0.0152
1-Propanol	1.3000	0.0299	3	60	0.0005	0.0003	0.0179
2-Butanol	0.5000	0.0115	4	74	0.0002	0.0001	0.0075
1-Butanol	0.6000	0.0138	4	74	0.0002	0.0001	0.0090
2-Pentanol	0.0000	0.0000	5	88	0.0000	0.0000	0.0000
1-Pentanol	0.0000	0.0000	5	88	0.0000	0.0000	0.0000
Water	89.6000	2.0608	0	18	0.1145	0.0795	0.0000
						Total in aqueous	0.0987
Total carbon due to oil and aqueous phase			2.7395 g carbon /day				

Catalyst stability testing in separate-bed , TOS = 24-48 h							
Base catalyst weight = 0.5 g, T=300°C , H ₂ /CO ratio = 1, total feed rate = 100 scc/min, reactor pressure = 300 psi,							
ZSM-5 weight = 1 g , Organic phase wt (24-48 h) = 7.62 g, Aqueous phase wt (24-48 h) = 2.3 g							
Aromatics	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
toluene	6.8455	0.5216	7	92	0.0057	0.0039	0.4763
p-xylene	11.0089	0.8389	8	106	0.0079	0.0055	0.7597
propylbenzene	8.4654	0.6451	9	120	0.0054	0.0037	0.5806
butylbenzene	1.3622	0.1038	10	134	0.0008	0.0005	0.0930
		0.0000					
n-praffins	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
n-C ₅	1.0289	0.0784	5	44	0.0018	0.0012	0.1069
n-C ₆	4.3825	0.3339	6	86	0.0039	0.0027	0.2796
n-C ₇	2.7556	0.2100	7	100	0.0021	0.0015	0.1764
n-C ₈	1.1798	0.0899	8	114	0.0008	0.0005	0.0757
n-C ₉	0.9667	0.0737	9	128	0.0006	0.0004	0.0622
n-C ₁₀	0.8891	0.0678	10	142	0.0005	0.0003	0.0573
n-C ₁₁	0.4850	0.0370	11	156	0.0002	0.0002	0.0313
n-C ₁₂	0.3497	0.0266	12	170	0.0002	0.0001	0.0226
n-C ₁₃	0.2169	0.0165	13	184	0.0001	0.0001	0.0140
n-C ₁₄	0.3071	0.0234	14	198	0.0001	0.0001	0.0199
n-C ₁₅	0.0596	0.0045	15	212	0.0000	0.0000	0.0039
n-C ₁₆	0.0373	0.0028	16	226	0.0000	0.0000	0.0024
n-C ₁₇₊	0.2703	0.0206	17	240	0.0001	0.0001	0.0175
i-paraffins	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
i-C ₅	1.2832	0.0978	5	44	0.0022	0.0015	0.1333
i-C ₆	2.4117	0.1838	6	86	0.0021	0.0015	0.1539
i-C ₇	13.9700	1.0645	7	100	0.0106	0.0074	0.8942
i-C ₈	12.9020	0.9831	8	114	0.0086	0.0060	0.8279
i-C ₉	8.4753	0.6458	9	128	0.0050	0.0035	0.5449
i-C ₁₀	7.8914	0.6013	10	142	0.0042	0.0029	0.5082
i-C ₁₁	3.7504	0.2858	11	156	0.0018	0.0013	0.2418
i-C ₁₂	4.4465	0.3388	12	170	0.0020	0.0014	0.2870
i-C ₁₃	2.2063	0.1681	13	184	0.0009	0.0006	0.1425
i-C ₁₄	1.3136	0.1001	14	198	0.0005	0.0004	0.0849
i-C ₁₅	0.3917	0.0298	15	212	0.0001	0.0001	0.0253
i-C ₁₆	0.1660	0.0126	16	226	0.0001	0.0000	0.0107
i-C ₁₇₊	0.2066	0.0157	17	240	0.0001	0.0000	0.0134
						Total in oil	6.6471
Alcohols	wt % in aqueous liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
Methanol	0.0000	0.0000	1	32	0.0000	0.0000	0.0000
Ethanol	0.0558	0.0000	2	46	0.0000	0.0000	0.0000
2-Propanol	0.2000	0.0000	3	60	0.0000	0.0000	0.0000
1-Propanol	0.5000	0.0000	3	60	0.0000	0.0000	0.0000
2-Butanol	0.3000	0.0000	4	74	0.0000	0.0000	0.0000
1-Butanol	0.0000	0.0000	4	74	0.0000	0.0000	0.0000
2-Pentanol	0.2000	0.0000	5	88	0.0000	0.0000	0.0000
1-Pentanol	0.1000	0.0000	5	88	0.0000	0.0000	0.0000
Water	98.6442	0.0000	0	18	0.0000	0.0000	0.0000
						Total in aqueous	0.0000
Total Carbon due to oil and aqueous phase			6.6471 g carbon /day				

Catalyst stability testing in separate-bed, TOS = 48-96 h Base catalyst weight = 0.5 g, T=300°C, H ₂ /CO ratio = 1, total feed rate = 100 scc/min, reactor pressure = 300 psi, ZSM-5 weight = 1 g, Organic phase wt (48-96 h) = 15.6 g, Aqueous phase wt (48-96 h) = 4.64 g							
Aromatics	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
toluene	3.5595	0.2776	7.0000	92.0000	0.0030	0.0021	0.2535
p-xylene	6.9342	0.5409	8.0000	106.0000	0.0051	0.0035	0.4898
propyl-benzene	5.4249	0.4231	9.0000	120.0000	0.0035	0.0024	0.3808
butyl-benzene	1.1981	0.0934	10.0000	134.0000	0.0007	0.0005	0.0837
		0.0000					
n-paraffins	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
n-C ₅	1.3533	0.1056	5.0000	44.0000	0.0024	0.0017	0.1439
n-C ₆	5.0000	0.3900	6.0000	86.0000	0.0045	0.0031	0.3265
n-C ₇	3.9000	0.3042	7.0000	100.0000	0.0030	0.0021	0.2555
n-C ₈	2.1479	0.1675	8.0000	114.0000	0.0015	0.0010	0.1411
n-C ₉	1.5243	0.1189	9.0000	128.0000	0.0009	0.0006	0.1003
n-C ₁₀	1.1072	0.0864	10.0000	142.0000	0.0006	0.0004	0.0730
n-C ₁₁	0.3472	0.0271	11.0000	156.0000	0.0002	0.0001	0.0229
n-C ₁₂	0.1124	0.0088	12.0000	170.0000	0.0001	0.0000	0.0074
n-C ₁₃	0.0673	0.0053	13.0000	184.0000	0.0000	0.0000	0.0045
n-C ₁₄	0.1384	0.0108	14.0000	198.0000	0.0001	0.0000	0.0092
n-C ₁₅	0.0363	0.0028	15.0000	212.0000	0.0000	0.0000	0.0024
n-C ₁₆	0.0424	0.0033	16.0000	226.0000	0.0000	0.0000	0.0028
n-C ₁₇₊	0.0000	0.0000	17.0000	240.0000	0.0000	0.0000	0.0000
i-paraffins	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
i-C ₅	4.1485	0.3236	5	44	0.0074	0.0051	0.4413
i-C ₆	2.9794	0.2324	6	86	0.0027	0.0019	0.1946
i-C ₇	17.8000	1.3884	7	100	0.0139	0.0096	1.1663
i-C ₈	16.2000	1.2636	8	114	0.0111	0.0077	1.0641
i-C ₉	10.8000	0.8424	9	128	0.0066	0.0046	0.7108
i-C ₁₀	6.8000	0.5304	10	142	0.0037	0.0026	0.4482
i-C ₁₁	3.4549	0.2695	11	156	0.0017	0.0012	0.2280
i-C ₁₂	3.0367	0.2369	12	170	0.0014	0.0010	0.2006
i-C ₁₃	0.8396	0.0655	13	184	0.0004	0.0002	0.0555
i-C ₁₄	0.6138	0.0479	14	198	0.0002	0.0002	0.0406
i-C ₁₅	0.2455	0.0191	15	212	0.0001	0.0001	0.0163
i-C ₁₆	0.1342	0.0105	16	226	0.0000	0.0000	0.0089
i-C ₁₇₊	0.0499	0.0039	17	240	0.0000	0.0000	0.0033
						Total in oil	6.8758
Alcohols	wt % in aqueous liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
Methanol	0.1200	0.0028	1	32	0.0001	0.0001	0.0010
Ethanol	0.0800	0.0019	2	46	0.0000	0.0000	0.0010
2-Propanol	0.2200	0.0051	3	60	0.0001	0.0001	0.0031
1-Propanol	0.1000	0.0023	3	60	0.0000	0.0000	0.0014
2-Butanol	0.0800	0.0019	4	74	0.0000	0.0000	0.0012
1-Butanol	0.0000	0.0000	4	74	0.0000	0.0000	0.0000
2-Pentanol	0.0000	0.0000	5	88	0.0000	0.0000	0.0000
1-Pentanol	0.0000	0.0000	5	88	0.0000	0.0000	0.0000
water	99.4000	2.3061	0	18	0.1281	0.0890	0.0000
						Total in aqueous	0.0066
Total carbon due to oil and aqueous phase			6.8824 g carbon /day				

Catalyst stability testing in separate-bed, TOS = 96-144 h Base catalyst weight = 0.5 g, T=300°C, H ₂ /CO ratio = 1, total feed rate = 100 scc/min, reactor pressure = 300 psi, ZSM-5 weight = 1 g, Organic phase wt (96-144 h) = 14.9 g, Aqueous phase wt (96-144 h) = 4.5 g							
Aromatics	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
toluene	2.2808	0.1699	7	92	0.0018	0.0013	0.1551
p-xylene	2.1947	0.1635	8	106	0.0015	0.0011	0.1481
propyl-benzene	2.2363	0.1666	9	120	0.0014	0.0010	0.1499
butyl-benzene	1.1550	0.0860	10	134	0.0006	0.0004	0.0771
		0.0000					
n-praffins	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
n-C ₅	2.2420	0.1670	5	44	0.0038	0.0026	0.2278
n-C ₆	8.1943	0.6105	6	86	0.0071	0.0049	0.5111
n-C ₇	2.3800	0.1773	7	100	0.0018	0.0012	0.1489
n-C ₈	3.1695	0.2361	8	114	0.0021	0.0014	0.1988
n-C ₉	0.5141	0.0383	9	128	0.0003	0.0002	0.0323
n-C ₁₀	1.3400	0.0998	10	142	0.0007	0.0005	0.0844
n-C ₁₁	0.0175	0.0013	11	156	0.0000	0.0000	0.0011
n-C ₁₂	0.0175	0.0013	12	170	0.0000	0.0000	0.0011
n-C ₁₃	0.0386	0.0029	13	184	0.0000	0.0000	0.0024
n-C ₁₄	0.0188	0.0014	14	198	0.0000	0.0000	0.0012
n-C ₁₅	0.0292	0.0022	15	212	0.0000	0.0000	0.0018
n-C ₁₆	0.0000	0.0000	16	226	0.0000	0.0000	0.0000
n-C ₁₇₊	0.0000	0.0000	17	240	0.0000	0.0000	0.0000
i-paraffins	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
i-C ₅	9.8570	0.7343	5	44	0.0167	0.0116	1.0014
i-C ₆	0.8322	0.0620	6	86	0.0007	0.0005	0.0519
i-C ₇	30.7700	2.2924	7	100	0.0229	0.0159	1.9256
i-C ₈	15.6975	1.1695	8	114	0.0103	0.0071	0.9848
i-C ₉	7.8118	0.5820	9	128	0.0045	0.0032	0.4910
i-C ₁₀	3.1319	0.2333	10	142	0.0016	0.0011	0.1972
i-C ₁₁	2.8223	0.2103	11	156	0.0013	0.0009	0.1779
i-C ₁₂	1.8802	0.1401	12	170	0.0008	0.0006	0.1187
i-C ₁₃	0.6705	0.0500	13	184	0.0003	0.0002	0.0424
i-C ₁₄	0.4627	0.0345	14	198	0.0002	0.0001	0.0292
i-C ₁₅	0.1818	0.0135	15	212	0.0001	0.0000	0.0115
i-C ₁₆	0.0565	0.0042	16	226	0.0000	0.0000	0.0036
i-C ₁₇₊	0.0000	0.0000	17	240	0.0000	0.0000	0.0000
						Total in oil	6.7764
Alcohols	wt % in aqueous liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
Methanol	0.2460	0.0055	1	32	0.0002	0.0001	0.0021
Ethanol	0.1000	0.0023	2	46	0.0000	0.0000	0.0012
2-Propanol	0.0000	0.0000	3	60	0.0000	0.0000	0.0000
1-Propanol	0.0000	0.0000	3	60	0.0000	0.0000	0.0000
2-Butanol	0.2000	0.0045	4	74	0.0001	0.0000	0.0029
1-Butanol	0.0000	0.0000	4	74	0.0000	0.0000	0.0000
2-Pentanol	0.2200	0.0050	5	88	0.0001	0.0000	0.0034
1-Pentanol	0.1000	0.0023	5	88	0.0000	0.0000	0.0015
Water	99.1340	2.2305	0	18	0.1239	0.0861	0.0000
						Total in aqueous	0.0090
Total carbon due to oil and aqueous phase			6.7854				

Catalyst stability testing in separate-bed, TOS = 144-192 h							
Base catalyst weight = 0.5 g, T=300°C, H ₂ /CO ratio = 1, total feed rate = 100 scc/min, reactor pressure = 300 psi,							
ZSM-5 weight = 1 g, Organic phase wt (144-192 h) = 14.04 g, Aqueous phase wt = 4.24 g							
Aromatics	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
toluene	2.2297	0.1565	7	92	0.0017	0.0012	0.1429
p-xylene	2.2517	0.1581	8	106	0.0015	0.0010	0.1432
propyl-benzene	0.9768	0.0686	9	120	0.0006	0.0004	0.0617
butyl-benzene	0.6449	0.0453	10	134	0.0003	0.0002	0.0405
n-praffins	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
n-C ₅	1.9413	0.1363	5	44	0.0031	0.0022	0.1858
n-C ₆	9.2000	0.6458	6	86	0.0075	0.0052	0.5407
n-C ₇	3.2000	0.2246	7	100	0.0022	0.0016	0.1887
n-C ₈	4.8503	0.3405	8	114	0.0030	0.0021	0.2867
n-C ₉	0.0623	0.0044	9	128	0.0000	0.0000	0.0037
n-C ₁₀	0.0177	0.0012	10	142	0.0000	0.0000	0.0011
n-C ₁₁	0.0194	0.0014	11	156	0.0000	0.0000	0.0012
n-C ₁₂	0.0270	0.0019	12	170	0.0000	0.0000	0.0016
n-C ₁₃	0.0288	0.0020	13	184	0.0000	0.0000	0.0017
n-C ₁₄	0.0204	0.0014	14	198	0.0000	0.0000	0.0012
n-C ₁₅	0.0376	0.0026	15	212	0.0000	0.0000	0.0022
n-C ₁₆	0.0669	0.0047	16	226	0.0000	0.0000	0.0040
n-C ₁₇₊	0.0000	0.0000	17	240	0.0000	0.0000	0.0000
i-paraffins	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
i-C ₅	5.0426	0.3540	5	44	0.0080	0.0056	0.4827
i-C ₆	5.9292	0.4162	6	86	0.0048	0.0034	0.3485
i-C ₇	32.1000	2.2534	7	100	0.0225	0.0156	1.8929
i-C ₈	15.1000	1.0600	8	114	0.0093	0.0065	0.8926
i-C ₉	6.8000	0.4774	9	128	0.0037	0.0026	0.4028
i-C ₁₀	4.3922	0.3083	10	142	0.0022	0.0015	0.2606
i-C ₁₁	2.3957	0.1682	11	156	0.0011	0.0007	0.1423
i-C ₁₂	1.3485	0.0947	12	170	0.0006	0.0004	0.0802
i-C ₁₃	0.7060	0.0496	13	184	0.0003	0.0002	0.0420
i-C ₁₄	0.3754	0.0263	14	198	0.0001	0.0001	0.0224
i-C ₁₅	0.1326	0.0093	15	212	0.0000	0.0000	0.0079
i-C ₁₆	0.0597	0.0042	16	226	0.0000	0.0000	0.0036
i-C ₁₇₊	0.0957	0.0067	17	240	0.0000	0.0000	0.0057
						Total in oil	6.1910
Alcohols	wt % in aqueous liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
Methanol	0.4000	0.0085	1	32	0.0003	0.0002	0.0032
Ethanol	0.7600	0.0161	2	46	0.0004	0.0002	0.0084
2-Propanol	0.1000	0.0021	3	60	0.0000	0.0000	0.0013
1-Propanol	0.0000	0.0000	3	60	0.0000	0.0000	0.0000
2-Butanol	0.2000	0.0042	4	74	0.0001	0.0000	0.0028
1-Butanol	0.0000	0.0000	4	74	0.0000	0.0000	0.0000
2-Pentanol	0.3000	0.0064	5	88	0.0001	0.0001	0.0043
1-Pentanol	0.1000	0.0021	5	88	0.0000	0.0000	0.0014
Water	98.1400	2.0806	0	18	0.1156	0.0803	0.0000
						Total in aqueous	0.0182
Total carbon due to oil and aqueous phase			6.2092 g carbon /day				

Catalyst stability testing in separate-bed, TOS = 192-240 h							
Base catalyst weight = 0.5 g, T=300°C, H ₂ /CO ratio = 1, total feed rate = 100 scc/min, reactor pressure = 300 psi,							
ZSM-5 weight = 1 g, Organic phase wt (192-240 h) = 13.68 g, Aqueous phase wt (192-240 h) = 3.92 g							
Aromatics	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
toluene	1.9753	0.1351	7	92	0.0015	0.0010	0.1234
p-xylene	2.2794	0.1559	8	106	0.0015	0.0010	0.1412
propyl-benzene	0.8475	0.0580	9	120	0.0005	0.0003	0.0522
butyl-benzene	0.3153	0.0216	10	134	0.0002	0.0001	0.0193
n-praffins	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
n-C ₅	1.7240	0.1179	5	44	0.0027	0.0019	0.1608
n-C ₆	10.4295	0.7134	6	86	0.0083	0.0058	0.5972
n-C ₇	2.2938	0.1569	7	100	0.0016	0.0011	0.1318
n-C ₈	7.5656	0.5175	8	114	0.0045	0.0032	0.4358
n-C ₉	0.2299	0.0157	9	128	0.0001	0.0001	0.0133
n-C ₁₀	0.1943	0.0133	10	142	0.0001	0.0001	0.0112
n-C ₁₁	0.0326	0.0022	11	156	0.0000	0.0000	0.0019
n-C ₁₂	0.0188	0.0013	12	170	0.0000	0.0000	0.0011
n-C ₁₃	0.0404	0.0028	13	184	0.0000	0.0000	0.0023
n-C ₁₄	0.0304	0.0021	14	198	0.0000	0.0000	0.0018
n-C ₁₅	0.0566	0.0039	15	212	0.0000	0.0000	0.0033
n-C ₁₆	0.0411	0.0028	16	226	0.0000	0.0000	0.0024
n-C ₁₇₊	0.0000	0.0000	17	240	0.0000	0.0000	0.0000
i-paraffins	wt% in Hydrocarbon liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
i-C ₅	5.7493	0.3932	5	44	0.0089	0.0062	0.5362
i-C ₆	0.7777	0.0532	6	86	0.0006	0.0004	0.0445
i-C ₇	36.9467	2.5272	7	100	0.0253	0.0175	2.1228
i-C ₈	10.4400	0.7141	8	114	0.0063	0.0044	0.6013
i-C ₉	8.3046	0.5680	9	128	0.0044	0.0031	0.4793
i-C ₁₀	5.3290	0.3645	10	142	0.0026	0.0018	0.3080
i-C ₁₁	2.2815	0.1561	11	156	0.0010	0.0007	0.1320
i-C ₁₂	1.2249	0.0838	12	170	0.0005	0.0003	0.0710
i-C ₁₃	0.4833	0.0331	13	184	0.0002	0.0001	0.0280
i-C ₁₄	0.3582	0.0245	14	198	0.0001	0.0001	0.0208
i-C ₁₅	0.0303	0.0021	15	212	0.0000	0.0000	0.0018
i-C ₁₆	0.0500	0.0034	16	226	0.0000	0.0000	0.0029
i-C ₁₇₊	0.0000	0.0000	17	240	0.0000	0.0000	0.0000
						Total in oil	6.0477
Alcohols	wt % in aqueous liquid phase	weight (g/day)	Carbon number	Molecular weight g/mol	mol/day	mmol/min	g carbon /day
Methanol	0.1200	0.0024	1	32	0.0001	0.0001	0.0009
Ethanol	0.0000	0.0000	2	46	0.0000	0.0000	0.0000
2-Propanol	0.1500	0.0029	3	60	0.0000	0.0000	0.0018
1-Propanol	0.3000	0.0059	3	60	0.0001	0.0001	0.0035
2-Butanol	0.1000	0.0020	4	74	0.0000	0.0000	0.0013
1-Butanol	0.6000	0.0118	4	74	0.0002	0.0001	0.0076
2-Pentanol	0.5000	0.0098	5	88	0.0001	0.0001	0.0067
1-Pentanol	0.6000	0.0118	5	88	0.0001	0.0001	0.0080
Water	97.6300	1.9135	0	18	0.1063	0.0738	0.0000
						Total in aqueous	0.0289
Total carbon due to oil and aqueous phase			6.0766 g carbon /day				

Addition of Zeolite ZSM-5 to an Iron-based Fischer-Tropsch Catalyst supported on Activated Carbon: Effect of Reactor Conditions

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