

# Quantitative Comparison of Zeolite Addition to Iron-Based Catalysts for Fischer-Tropsch Synthesis in a Separate vs Mixed Reactor Bed Setup

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**Received:** December 05, 2020**Accepted:** December 16, 2020**Published:** December 18, 2020

**Citation:** Karre AV and Kababji AH. 2020. Quantitative Comparison of Zeolite Addition to Iron-Based Catalysts for Fischer-Tropsch Synthesis in a Separate vs Mixed Reactor Bed Setup. *J Appl Cat Chem Eng* 1(1): 11-16.

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## Abstract

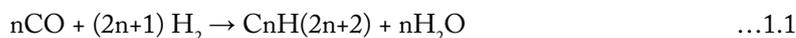
The delta quantities of gas and liquid products, rate of water-gas-shift and Fischer-Tropsch reactions are studied using iron (Fe) based Fischer-Tropsch (FT) catalysts promoted with metals such as Mo, Cu, and K supported on activated carbon (AC) along with ZSM-5 catalyst in a separate and a mixed bed reactor bed arrangement to investigate the benefits of bed arrangements. The delta amounts of different products are compared for the fixed amount of the base catalyst and the ZSM-5 amount is varied between 25, 50, and 100%. The purpose of this paper is to quantitatively compare both the beds to find out whether there is any improvement in the product distribution by changing the bed arrangement. The delta values are generally positive in the separate bed indicating a higher activity towards lower chain, isomers, and aromatic molecules compared to mixed bed arrangement. The delta values of alcohols are generally negative indicating that the ZSM-5 catalyst and the base catalyst have reduced their activities in the mixed bed arrangement. In addition, the base catalyst and ZSM-5 in the mixed bed showed a reduction in activity mainly due to metal migration of the base catalyst to ZSM-5 and coke formation on ZSM-5.

## Keywords

Cobalt, Iron, Fischer-Tropsch, ZSM-5, Activated carbon

## Introduction

Fischer-Tropsch synthesis (FTS) is a catalytic process where the reaction of carbon monoxide (CO) and hydrogen (H<sub>2</sub>) gas forms hydrocarbons and oxygenate compounds. The main reaction for FTS is the production of hydrocarbon through a polymerization chain reaction mechanism, shown by [equation 1.1](#) [1, 2].



The other important reaction especially over the iron-based catalyst is the water gas shift reaction (WGS) shown by [equation 1.2](#) [1, 2].



The Fischer-Tropsch (FT) process was invented by German scientists Franz Fischer and Hans Tropsch. They used the FT technology during World War II to satisfy great amount of fuel demand [3]. After World War II, most of these plants were dismantled and shut down for economic reasons [3]. Today, the FT process is commercially used by a limited number of operating companies in few locations such as Sasol in South Africa. FT synthesis mainly uses cobalt- (Co) and iron-based catalyst commercially. Cobalt is 1000 times more expensive than iron. Cobalt-based catalysts are only used in the Low-Temperature Fischer-Tropsch (LTFT) process and produces excessive methane at higher temperatures

[4]. The Fe-based FT catalyst process employs low  $H_2/CO$  ratios, whereas the Co-based FT catalyst process requires higher ratio [5].

FT synthesis mainly suffers from polymerization kinetics which leads to waxy products. Waxy products are long-chain hydrocarbons i.e. greater than  $C_{20}$  [6]. Hence, the long-chain length of hydrocarbons is further converted into shorter-range of hydrocarbons such as gasoline [7]. Martinez et al., [6] used zeolite (USY-500, USY-720, H-Beta, H-MOR, and HZSM-5) and cracked FT produced long-chain hydrocarbons to gasoline- and diesel-range products. Ma et al., [7] have shown that the chain length of FT liquid products could be controlled below  $C_{20}$  over an activated carbon support. In this study, zeolite and activated carbon along with iron-based promoted catalyst are used for tailoring hydrocarbon products.

A multi-metal iron-based catalyst supported on activated carbon is used as a base reference catalyst. ZSM-5 zeolite is used as an acidic catalyst to crack, isomerize, aromatize, and oligomerize FT products produced by the base catalyst. Cracking reaction converts waxy chain hydrocarbon molecules to smaller chains. Isomerization reaction converts straight chain hydrocarbon chains to isomers by rearranging  $-CH_3$  group. Oligomerization reaction removes hydrogen atoms from the straight chain hydrocarbons to form olefinic compound of the same carbon chain. Aromatization reaction converts oligomers produced to aromatic hydrocarbons. Previously, two types of bed arrangements were studied, one is separate bed where ZSM-5 is located after the base catalyst and the second arrangement is the mixed bed where the ZSM-5 is uniformly mixed with the base catalyst. The weight ratio of ZSM-5 to the base catalyst weight is varied for both the bed arrangement and performance results were analyzed. The goal of this paper is to perform a quantitative comparison of both the bed arrangements and see if there is any improvement in product selectivity, product amounts, and reaction rates.

## Material and Methods

### Catalyst preparation

Norit SX Ultra activated carbon (AC) was purchased from Sigma Aldrich and used as metal support for the FT catalyst. The base prepared catalyst contained 16 parts Fe, 6 parts Mo, 0.9 parts K and 0.8 parts Cu in 100 parts of AC. Metal promoters were added to AC support sequentially via the incipient wetness impregnation (IWI) method, with drying between impregnations. The drying in air was carried out overnight at 90-100°C. The ZSM-5 (CBV 5524-G) was obtained from Zeolyst International and the 20-40 mesh was prepared. More details can be found in Karre et al. [8].

### Reaction equipment

A schematic of the reactor system setup is shown in figure 1. There are three gas cylinders connected to the reactor system: helium, hydrogen, and syngas (45% $H_2$ , 45% $CO$ , 5% $He$ , 5% $Ar$ ). These gases are fed into the catalyst bed through a separate mass flow controllers (MFCs), model No. 5850 E and manufactured by Brooks Instruments. The MFC's

has operating range of 0-200 cc/min. The reactor is a fixed-bed stainless-steel tube with a jacketed furnace, supplied by Applied Test Systems, to maintain the temperature. The reactor consists of a stainless-steel tube (SS 304L), made of TW metal, of outer diameter 0.5 in., tube length 25 in., and wall thickness 0.049 in. 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 temperature is controlled using a software InTouch by Wonderware. Thermocouples are placed the middle of the catalyst bed to monitor the catalyst bed temperature. The reactor contains the catalyst mixture in the center, with 1/16" quartz chips placed upstream and downstream in the catalyst bed. The reactor is pressured manually, and the pressure is maintained by the back-pressure regulator (BPR). An auto-injection gas sampler is available for the PerkinElmer gas chromatography (GC) and is controlled from the computer. Liquid samples collected are analyzed offline by an offline Varian GC.

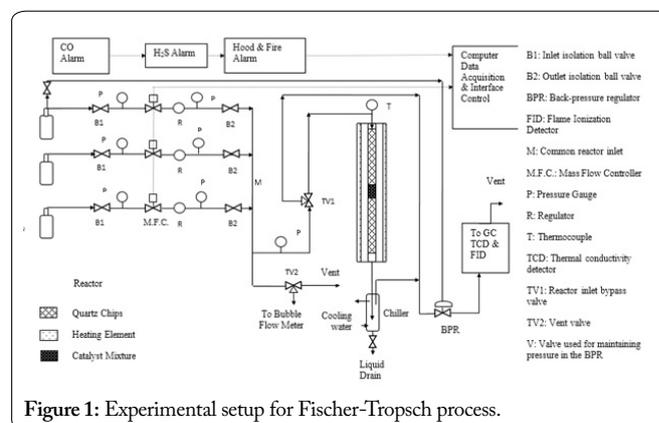


Figure 1: Experimental setup for Fischer-Tropsch process.

### Experimental procedure

For mixed bed arrangement, 0.5 g of the base catalyst is mixed with different weights of ZSM-5 (0.25, 0.5, and 1 g) for different experiments and diluted with 4 g of 1/32-inch quartz chips (1:4wt dilution). For separate bed arrangement, 0.5 g of the base catalyst is placed first followed by different weights of ZSM-5 (0.25, 0.5, and 1 g) to perform the additional experiments, both the catalysts were diluted with 1/32-inch quartz chips (1:4wt dilution) and separated by quartz wool. Catalyst activation is done by passing 200 cc/min of hydrogen gas at 400°C for 12 h. The reactor is maintained with following conditions:  $H_2/CO$  ratio = 1, total feed rate = 100 scc/min, temperature = 300°C, pressure = 300 Psi. Each reaction was allowed to run for 72 h and liquid samples collected every 24 h. A liquid sample of time on stream (TOS) between 24-48 h is analyzed for all reactions. The liquid, which has two phases, is collected in a 25-ml vial. One phase is organic (oil) and other is aqueous. The oil phase, being less dense compared to the aqueous phase, is carefully removed with an Eppendorf-type pipette, and the weight of both the samples (oil and aqueous phases) is measured.

### Characterization equipment

Scanning Electron Microscopy (SEM), by a Hitachi S-4700 scanning electron microscope at an accelerated voltage of 10 kV, was used that gives information about the

surface morphology of a sample. Temperature-Programmed Reduction (TPR) is used to find the degree of reduction of the catalyst. 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.

### Methodology of calculations and analysis

The distribution of individual products from the separate bed and the mixed bed has already been discussed separately in previous work by Karre et al. [8, 9]. The purpose of this paper is to quantitatively compare both the beds to find out whether there is any improvement in the product distribution by changing the bed arrangement. For quantitative analysis, the changes in amounts (X) of different items such as gaseous hydrocarbons, liquid hydrocarbons, and aqueous products are calculated with changing reactor configuration. A term delta value is defined as;

$$\Delta X = (X \text{ in separate-bed catalyst arrangement}) - (X \text{ in the mixed-bed catalyst arrangement}) \dots 1.3$$

## Results and Discussion

### Catalyst characterization

Figure 2 shows EDX analysis of spent ZSM-5 in the separate bed after 72 h. Au and Pd are the coating material used in the EDX analysis. As mentioned earlier in [8, 9], the amount of carbon as coke is not detected on the fresh ZSM-5 sample. And as per Figure 2, coke presence on the spent ZSM-5 catalyst indicates that the ZSM-5 has been significantly degraded or masked is probably due to heavy waxy hydrocarbon molecules. Also, from figure 2, absence of Fe, Cu, K, or Mo metal on the ZSM-5 indicates that metal migration from the base catalyst to ZSM-5 did not happen in the separate bed.

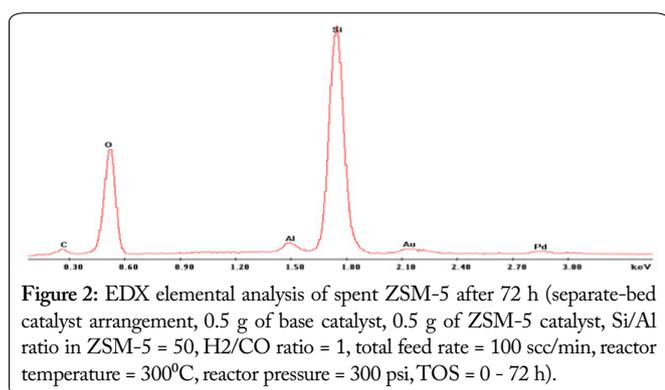


Figure 2: EDX elemental analysis of spent ZSM-5 after 72 h (separate-bed catalyst arrangement, 0.5 g of base catalyst, 0.5 g of ZSM-5 catalyst, Si/Al ratio in ZSM-5 = 50, H<sub>2</sub>/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 psi, TOS = 0 - 72 h).

Figure 3 shows EDX analysis of spent ZSM-5 in the mixed bed after 72 h. Figure 3 confirms the presence of carbon as well as Fe and Cu metals. The higher concentration of coke in figure 3 compared to figure 2 signifies that the coke quantity formed on the ZSM-5 surface in the mixed bed configuration is higher. Also, as per figure 3, metals such as Fe and Cu on ZSM-5 surface indicate that metals are migrated from the base catalyst to the ZSM-5 catalyst, this decreased the activity of the base catalyst in the mixed bed arrangement.

B.E.T. surface area measurement is done for Norit SX Ultra activated carbon and compared with the value found by Ma et al [10]. Based on below data, the B.E.T. surface area measured for Norit SX Ultra activated carbon is consistent with the value measured by Ma et al [10].

B.E.T. surface area = 927 m<sup>2</sup>/g (Surface area measured for Norit SX Ultra)

B.E.T. surface area = 1,016 m<sup>2</sup>/g [10]

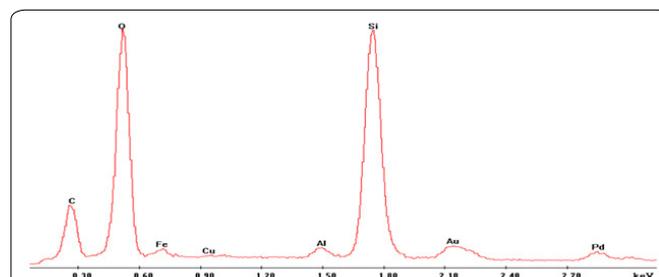


Figure 3: EDX elemental analysis of spent ZSM-5 after 72 h (mixed-bed catalyst arrangement, 0.5 g of base catalyst, 0.5 g of ZSM-5 catalyst, Si/Al ratio in ZSM-5 = 50, H<sub>2</sub>/CO ratio = 1, total feed rate = 100 scc/min, reactor temperature = 300°C, reactor pressure = 300 psi, TOS = 0 - 72 h).

### Delta values of overall products

Table 1 shows the delta amounts of overall products calculated using equation 1.3. The delta values of overall products are shown in table 1. The delta values of C<sub>1</sub>, C<sub>2</sub>-C<sub>4</sub>, and total C<sub>5+</sub>, are positive for all the ZSM-5 amounts implying that the separate-bed is efficient in producing these hydrocarbons compared to mixed bed. This is because the activity of the base catalyst is reduced to higher extent in the mixed bed arrangement compared to separate bed arrangement due to alkali metal migration from the base catalyst to ZSM-5. The negative values of alcohols indicate that all the alcohols molecules produced by the base catalyst in the separate bed are converted to hydrocarbons and water over the ZSM-5 catalyst. Moreover, all the alcohols produced by the base catalyst in the base catalyst in the mixed bed did not

Table 1: Delta amounts of overall products (0.5 g of base catalyst, Si/Al ratio in ZSM-5 = 50, H<sub>2</sub>/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
Relative ZSM weight (%)	25	50	100
<b>Compounds</b>	$\Delta$ (Compound) g carbon/day		
C <sub>1</sub>	0.75	0.87	0.54
C <sub>2-4</sub>	1.6	2.2	2.08
Sum of C <sub>1-4</sub> (Gas)	2.35	3.07	2.62
Total C <sub>5+</sub> (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 <sub>2</sub>	5.71	4.76	1.54
Unreacted CO	-10.56	-10.68	-3.46

convert due to the reduced activity of coked ZSM-5 catalyst. Also, the delta values of  $C_1$ ,  $C_2$ - $C_4$ , and sum of gas + liquid are highest for ZSM-5 = 0.5 g and then further decreased with further ZSM-5 loading. This suggests that the 50% ZSM-5 sample is optimal in a separate bed arrangement and further increase in ZSM-5 loading increases the coking of ZSM-5, also explained in section 3.6. The delta value for alcohol with 25% ZSM-5 is most negative indicating that the ZSM-5 in the mixed bed arrangement was not able to completely convert alcohols due to reduced activity and lower acidic sites compared with ZSM-5 = 0.5 g.

From table 1, 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 FTS conversion happened over the base catalyst in the separate bed arrangement. Higher  $CO_2$  is produced because higher quantity of CO is reacted in the separate bed arrangement. On the contrary, the base catalyst in the mixed bed showed lower activity towards  $CO_2$  production and CO conversion due to alkali migration from the base catalyst to the ZSM-5. The delta amounts of  $CO_2$  produced is decreased with increasing ZSM-5 loading. This suggests that the alcohols produced on the base catalyst are dehydrated more with increasing ZSM-5 amount, and also water was utilized by WGS reaction over the base catalyst to produce more  $CO_2$ .

### Delta values of WGS and FTS reaction activities

Table 2 shows the rates of WGS and FTS calculated using equation 1.3. The delta rates of WGS and FTS are positive for all the ZSM-5 amounts. This means that the activities of WGS and FTS are higher for the base catalyst in separate bed compared to mixed bed. The reduced activity of the base case catalyst in the mixed bed is due to the alkali migration to ZSM-5. On the contrary, the alkali migration from the base catalyst to ZSM-5 did not take place in the separate bed. The delta rates of WGS for the both the arrangements is nearly same for ZSM-5 weight of 1 g, this could be due to combination of dehydration reactions on ZSM-5 and WGS reactions on the base catalyst.

**Table 2:** Delta amounts of WGS and FTS reaction rates (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).

ZSM-5 weight (g)	0.25	0.5	1
<b>Rates</b>	$\Delta$ (Rate) mmol/min		
<b>rWGS</b>	0.33	0.27	0.09
<b>rFTS</b>	0.36	0.35	0.15

### Delta amounts of gas products

Table 3 shows the delta amounts of  $CH_4$ ,  $C_2H_6 + C_2H_4$ ,  $C_3H_8$ ,  $C_3H_6$ ,  $i-C_4H_{10}$ ,  $n-C_4H_{10}$ ,  $1-C_4H_8$ ,  $i-C_4H_8$ ,  $t-C_4H_8$ ,  $c-C_4H_8$ ,  $i-C_5H_{12}$ ,  $n-C_5H_{12}$ , and  $C_5$ -gas hydrocarbons calculated using equation 1.3.

From table 3, the delta amounts of  $CH_4$ ,  $C_2H_6 + C_2H_4$ ,  $C_3H_8$ ,  $i-C_4H_{10}$ ,  $n-C_4H_{10}$ ,  $1-C_4H_8$ ,  $i-C_4H_8$ ,  $i-C_5H_{12}$ , and  $n-C_5H_{12}$  are

**Table 3:** Delta amounts of gas products (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).

ZSM-5 weight (g)	0.25	0.5	1
<b>Products</b>	$\Delta$ (Product) g carbon/day		
<b><math>CH_4</math></b>	0.75	0.87	0.54
<b><math>C_2H_6 + C_2H_4</math></b>	0.88	0.89	0.58
<b><math>C_3H_8</math></b>	0.32	0.99	1.22
<b><math>C_3H_6</math></b>	-0.41	-0.50	-0.57
<b><math>i-C_4H_{10}</math></b>	0.22	0.57	0.92
<b><math>n-C_4H_{10}</math></b>	0.24	0.68	0.73
<b><math>1-C_4H_8</math></b>	-0.16	-0.20	-0.14
<b><math>i-C_4H_8</math></b>	0.59	-0.09	-0.41
<b><math>t-C_4H_8</math></b>	-0.04	-0.06	-0.15
<b><math>c-C_4H_8</math></b>	-0.04	-0.09	-0.09
<b><math>i-C_5H_{12}</math></b>	0.14	0.41	0.42
<b><math>n-C_5H_{12}</math></b>	0.17	0.15	0.19
<b><math>C_5</math>-gas</b>	-0.02	-0.29	-0.30

positive indicating that higher amount of these hydrocarbons in the separate bed is produced due to cracking and isomerization reactions over the ZSM-5. Cracking reactions break down larger hydrocarbon molecule into smaller chain and isomerization reaction rearranges a straight chain hydrocarbon molecule into isomer. The delta amount of  $CH_4$  is highest for the separate bed arrangement with 50% ZSM-5 loading and lowest for 100% ZSM-5 loading. This means that at 50% ZSM-5 loading in the separate bed arrangement, cracking reaction are favorable towards production of  $CH_4$  gas and with additional ZSM-5 loading  $CH_4$  molecules are converted to other mid-range hydrocarbons due to availability of higher acidic sites in the separate bed arrangement. These reactions occur to a lower extent in the mixed bed because of reduced ZSM-5 activity due to metal migration and coking. The negative delta values for  $C_3H_6$ ,  $1-C_4H_8$ ,  $t-C_4H_8$ ,  $c-C_4H_8$ , and  $C_5$ -gas (higher amounts in the mixed bed) are due to the decrease of oligomerization active site on ZSM-5 in that configuration. Oligomerization reaction rearranges an olefin molecule into either isomer or a straight chain hydrocarbon. The decrease in these active sites as evidenced EDX elemental analysis (Figures 2 and 3) in the mixed bed is due to alkali migration from the base catalyst to the ZSM-5. The increase in amounts of  $i-C_4H_{10}$  and  $i-C_5H_{12}$  with increasing ZSM-5 loading in the separate bed is due to increase in isomerization active sites. The activity of isomerization active sites is decreased in the mixed bed arrangement due to alkali metal migration and higher amount of coking on ZSM-5 catalyst.

### Delta amounts of overall liquid production rates

Table 4 shows the delta amounts of overall hydrocarbon and overall alcohol production rates calculated using equation 1.3.

From table 4, the delta amounts of hydrocarbon production are shown for all the ZSM-5 amounts. The delta amount for

**Table 4:** Delta amounts of hydrocarbon and alcohol production rates (0.5 g of base catalyst, Si/Al ratio in ZSM-5 = 50, H<sub>2</sub>/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
<b>Production rates</b>	Δ (Rate) g/Kg FT cat./h		
<b>Hydrocarbon production</b>	295.00	265.00	215.83
<b>Alcohol production</b>	-50.82	-56.79	-19.31

hydrocarbons is highest for 25% ZSM-5 loading and decrease with further increase in ZSM-5 loading. As the quantity of base catalyst used is fixed for all the reactions, the yield of liquid hydrocarbons produced should be constant without ZSM-5. But since ZSM-5 is utilized in all the reactions it changes the liquid and gas distribution through various reactions. So, a small quantity of ZSM-5 is sufficient in the separate bed arrangement to maximize yield of liquid hydrocarbons through several reactions over ZSM-5 catalyst and higher quantity of ZSM-5 leads to cracking of liquid hydrocarbons into smaller chain hydrocarbons. Since more acid active sites are available in the separate bed compared with mixed bed arrangement and also the activity of the base catalyst in the mixed bed is reduced due to metal migration, the delta values of hydrocarbons are positive. Also, the amount of alcohols produced in the mixed bed is higher compared with the base catalyst. This is because the activity of the base catalyst in the mixed bed is reduced due to metal migration to ZSM-5. The delta values of alcohols produced is more negative with smaller ZSM-5 loading compared with highest, the data indicate that, for a mixed bed arrangement, higher quantities of ZSM-5 active sites probably be available at higher ZSM-5 loading. The activity of ZSM-5 to convert alcohols to hydrocarbons and water is decreased in the mixed bed due to metal migration and increased coking. For the separate bed arrangement, all the alcohols produced by the base catalyst are reacted over the ZSM-5 catalyst, also mentioned previously by Karre et al. [9].

### Delta amounts of hydrocarbons in organic liquid phase

Table 5 shows the delta amounts of liquid hydrocarbons calculated using equation 1.3. From table 5, the delta amounts of n-paraffins with carbon chain from 5 to 14 are generally positive for ZSM-5 weight of 0.25 g and 0.5 g. Higher than ZSM-5 weight of 1 g leads to cracking, isomerization, aromatization of n-C<sub>6</sub>-C<sub>10</sub> hydrocarbon chains into toluene and p-xylene molecules. The negative delta values of n-C<sub>15+</sub> for ZSM-5 weight 0.25 g and 0.5 g suggests that the activity of the base catalyst in the mixed bed is reduced due to alkali metal migrations and also the ability of ZSM-5 to crack heavy chain molecules is reduced due to coking and reduced active sites of alkali metal transfer. The delta amounts of i-C<sub>5</sub>-C<sub>8</sub> is much greater for ZSM-5 weight of 0.25 g than other cases suggesting that the separate bed arrangement is more active towards producing higher content of gasoline range isomers. Further increase in ZSM-5 loading shifts the product profile from i-C<sub>5</sub>-C<sub>8</sub> to more aromatic compounds. This is mainly because more aromatization actives sites are available with increase in ZSM-5 weight. The extent of aromatization in the separate bed is higher than the mixed bed suggesting that the

activity of ZSM-5 is reduced in the mixed bed due to alkali metal migration and coking. The delta amounts of i-C<sub>9</sub>-C<sub>13</sub> is maximum for the separate bed for ZSM-5 weight of 0.5 g, suggesting that the ZSM-5 activity in mixed bed is reduced due to coking and alkali metal transfer.

From table 5, the delta amounts of liquid aromatics are generally low or insignificant 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.

**Table 5:** 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, H<sub>2</sub>/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
<b>n-paraffins</b>	Δ (n-paraffin) mg carbon/day		
n-C <sub>5</sub>	60.9	59	66.3
n-C <sub>6</sub>	136.4	134.8	-42.3
n-C <sub>7</sub>	338	33.5	-80.1
n-C <sub>8</sub>	152	5.5	-39.1
n-C <sub>9</sub>	87.3	6.4	-24.7
n-C <sub>10</sub>	76.7	16.3	-15.2
n-C <sub>11</sub>	68.7	25.7	7.1
n-C <sub>12</sub>	11.5	3.9	-0.9
n-C <sub>13</sub>	3.1	-4.7	-2.9
n-C <sub>14</sub>	11.9	1.8	11.2
n-C <sub>15</sub>	-4.3	-7.1	2.8
n-C <sub>16</sub>	-7.5	-7.8	2.7
n-C <sub>17+</sub>	-10.2	-21.8	1.6
<b>i-paraffins</b>	Δ (i-paraffin) mg carbon/day		
i-C <sub>5</sub>	148	-6.9	333.7
i-C <sub>6</sub>	52.3	50.8	95.2
i-C <sub>7</sub>	985.1	320	73.8
i-C <sub>8</sub>	606.7	299.1	-25
i-C <sub>9</sub>	176.7	238.2	126.1
i-C <sub>10</sub>	102	200.2	185.4
i-C <sub>11</sub>	21.3	79.9	62.7
i-C <sub>12</sub>	27.6	190.1	90.4
i-C <sub>13</sub>	8.5	90.4	83.3
i-C <sub>14</sub>	6.4	48.5	65.1
i-C <sub>15</sub>	4.5	12.2	30.5
i-C <sub>16</sub>	9.3	-0.7	18.7
i-C <sub>17+</sub>	-1.9	-3.9	8.3
<b>Aromatics</b>	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

The overall reaction sequence in 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.

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

Table 6 shows the delta amounts of alcohol products and water in the aqueous liquid phase calculated using equation 1.3.

From table 6, the delta amounts of all alcohol products and water are generally negative for all the ZSM-5 amounts used, except for 2-pentanol. Higher amount of alcohols is remained unconverted in the mixed bed compared to separate bed. This is because all the alcohols formed by the base catalyst in the separate bed pass through completely over the ZSM-5 but the same is not true for the mixed bed. Moreover, the ZSM-5 activity in the mixed bed is reduced due to alkali metal migration and increased coke formation. Higher amount of water is produced in the separate bed compared to mixed bed because all the alcohols formed in separate bed is converted to hydrocarbons and water.

**Table 6:** 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, H<sub>2</sub>/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
<b>Aqueous product</b>	$\Delta$ (Product) mg carbon/day		
<b>Methanol</b>	-47.3	-47.8	-24.2
<b>Ethanol</b>	-129	-141.8	-49.2
<b>2-Propanol</b>	32.3	-23.8	-13.9
<b>1-Propanol</b>	-70.6	-61.2	-17.9
<b>2-Butanol</b>	-1.8	-10.7	-4.8
<b>1-Butanol</b>	-60.7	-60.3	-9
<b>2-Pentanol</b>	0.1	0	0
<b>1-Pentanol</b>	-52.4	-21.5	0
	$\Delta$ (Product) mg/day		
<b>Water</b>	1809.9	1294.5	45.4

### Summary and Conclusion

Overall, positive delta values of product amounts in the separate bed showed higher activity than the mixed bed because of alkali metal migration from the base catalyst to the ZSM-5 and higher coking as evidenced by EDX elemental analysis. The separate bed arrangement did not exhibit any alkali metal transfer but showed lower coking potential compared to mixed bed. A positive delta values reaction rates indicate that the activity of the base catalyst in the mixed bed is much lower compared to separate bed mainly due to the alkali metal transfer.

The negative delta values of the alcohols indicate that the alcohols produced in the separate bed are all converted to hydrocarbons and water due to higher activity of ZSM-5. By increasing the ZSM-5 loading in the mixed bed the delta values have approached towards zero, further indicating that mixed bed is not effective in converting alcohols produced by the Fischer-Tropsch reactions. The delta values are generally positive indicating that the cracking, isomerization, oligomerization, aromatization, and dehydrations reactions are enhanced with increasing ZSM-5 loading in the separate bed arrangement. Higher delta amounts of aromatic molecules formed at higher loading of ZSM-5 leads to formation of coke on the ZSM-5 surface. Overall, the separate bed arrangement showed higher amounts of desired products compared with mixed bed.

### Acknowledgments

This study was supported by the U.S. Department of Energy under a Cooperative Agreement DE-FC26-05NT42456 with the Consortium for Fossil Fuel Science (CFFS). The funding source played no role in the study's design; in the collection, analysis and interpretation of the data; in report writing; or in publication decisions.

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