STUDIES ON CATALYTIC AROMATIZATION OF YANHUA FCC GASOLINE FRACTIONS

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Keywords: aromatization reaction; reaction condition; FCC gasoline; Yanhua; LPG

By using Yanhua FCC gasoline and a fraction of Yanhua FCC gasoline (boiling point < 90 °C) as a feedstock, the effects of reaction temperature, Weight Hour Space Velocity (WHSV), and feedstock performance on yields of LPG, aromatics and propylene production were studied in a confined fluidized bed reactor. The experimental results show that yields of aromatics, propylene, and aromatics + propylene for both Yanhua FCC gasoline and the selected fraction of Yanhua FCC gasoline increase with the increase of reaction temperature at the same WHSV. Yields of aromatics, propylene and aromatics+propylene decrease with the increase of WHSV at the same reaction temperature.

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Introduction

With increasing the requirements of environmental regulations to petroleum products, United States, Japan and other European countries[1] issued a new gasoline standard to decrease the olefin contents of gasoline, towards 25% (by volume) or even lower.[2] A new gasoline standard was put in practice from January 2003 in China because of the requirement of environmental protection.[3] As requested, the content of olefins, sulfur, benzene and other aromatic compounds had to be lower than 35 % (v/v), 0.08 % (m/m), 2.5 % (v/v) and 40 % (v/v), respectively, and the research octane number (RON) was required to be above 90[4]. Owing to the enforcement of the new standards, all refineries have to face the challenge.[5] Nowadays, however, the portion of FCC (fluid catalytic cracking) gasoline in commercial gasolines is about 85 % (m/m) and their olefin concentration is roughly between 50 and 60 % (m/m) inspite of the improvement of fluid catalytic cracking technologies in China. Consequently, the average olefin content of gasoline measured in 60 refinery plants reaches 44.2%, opposite to the requirements of the new standards.[6] In order to satisfy the new Chinese Standard requirements, numerous new aromatization catalysts were studied.[7] Using these new catalysts the olefin content of gasoline could be transformed into a mixture of i-paraffins and aromatic compounds, which gradually improves the stability of gasolines and decreases their harmfully emitted amounts in the tail gas of cars, and ensures the appropriate gasoline octane number as well.[8]

In this paper, the distribution of aromatization reaction products of Yanhua FCC gasoline formed under different reaction conditions in a confined fluidized bed reactor is discussed.

EXPERIMENTAL

Feedstock

Yanhua FCC gasoline was obtained from an FCC Unit of Yanhua Petrochemical Company. The composition of gasoline fractions are shown in Table 1. The FCC gasoline was obtained from the Heavy Oil Fluid Catalytic Cracking Unit and was not treated at all, not hydrorefined and desulfurized, therefore it has high olefin content.

Table 1 Composition of Yanhua FCC gasoline and the selected fraction (b.p.<90 °C) of Yanhua FCC gasoline (%, v/v)

Feedstock	Yanhua FCC gasoline	The Yanhua FCC gasoline fraction
n-Paraffins	3.02	4.92
i-Paraffins	20.41	30.28
c-Paraffins	5.29	4.36
Olefins	51.47	57.69
Aromatics	19.81	2.75
Total	100.0	100.0

Catalyst

LBO-A catalyst (Pt/HZSM-5 (Si/Al=38) type), which was aged with 2 ml min^{-1} steam at 800 °C in a confined fluidized bed reactor, was obtained from Lanzhou Petrochemical. Its properties are shown in Table 2.

Table 2. Properties of LBO-A catalyst

Parameters	Value
Micro-activity Test Index (MATI), %	56
Apparent density, g/ml	0.8
Pore volume, ml/g	0.3
Surface area, m^2/g	85
Particle size distribution, % (by mass)	
<45.8 μm	20.6
45.8~111.0 μm	60.3
>111.0 μm	19.1

The micro-activity test index (MATI) was obtained by using a micro-reactor and light oil provided by Beijing Petroleum Chemical Institute with distillation range of 225 to 337 °C. The reaction temperature, reaction time, inflow oil amount, and catalyst weight in the micro-reactor were kept to be stable, namely 460 °C, 70 s, 1.56 g and 5.0030 ± 0.0010 g, respectively.

The liquid products of above reaction were distilled out and analyzed by using an SP 3420 Gas Chromatograph. MATI values are given as follows:

$$M = 1 - \frac{(m*W_2)}{m_1} \qquad (1)$$

where *M* is MATI value, %; *m* is liquid product weight, g; m_1 is the total inflow oil weight, g; W_2 is the mass fraction of diesel oil in the liquid product.

Apparatus

A confined fluidized bed reactor shown in Fig.1. was used in Yanhua FCC gasoline aromatization process. The instrument consists of five parts: oil and stream input system, reaction zone, temperature control, product separation, and collection system. Variable amount of distilled water was pumped into the furnace to evaporate and form steam, then the steam was mixed with the Yanhua FCC gasoline pumped by an other pump simultaneously at the outlet of a constant temperature box. The mixture was heated to approximately 450 °C in a preheated room before it entered the reactor.

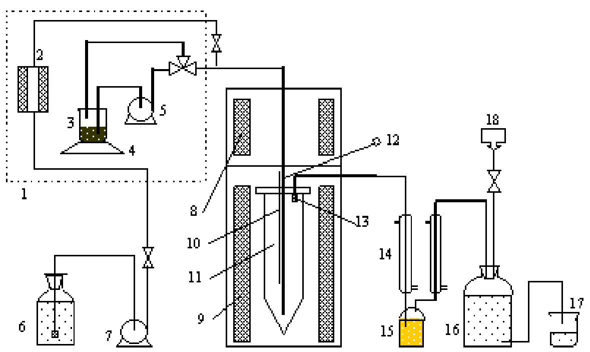

Fig.1 Schematic drawing of experimental apparatus

1-constant temperature room; 2-steam furnace; 3-feedstock; 4-electronic scale; 5-gasoline pump; 6-water tank; 7-water pump; 8-preheated room; 9-furnace; 10-thermocouple; 11-reactor; 12-catalyst inlet; 13-filter; 14-condenser; 15-liquid product collection bottle; 16-gas collection bottle; 17-beaker; 18-gas sample bag

Analytical methods

An HP6890 Gas Chromatograph with ChemStation software was used to measure the volume percentage of aromatizated gas components. The measured data were converted to mass percentage using the equation of state for ideal gases. The aromatized liquid was analyzed with TSY-1132 （Measure Coke Equipment） to obtain the mass percentage of paraffins, olefins, and aromatics. The mass percentage of coke on catalyst was measured with KJ-02 Fast and Exact Measuring Coke Equipment.

RESULTS AND DISCUSSION

Effects of reaction temperature and WHSV on the yield of products formed from Yanhua FCC gasoline

Table 3 shows the relations between reaction temperature, WHSV and the yields of reaction products formed from Yanhua FCC gasoline. When WHSV increased, gasoline had less contact time with the catalyst. It means that gasoline had not much time to react with the catalyst, so yields of off-gas, LPG and coke decreased with the increase of WHSV at the same reaction temperature, but yield of light oil increased with the increase of WHSV at the same reaction temperature. When reaction temperature increased, the catalytically active energy content of the system increased. It means that the probability of the crack reactions increased. The experimental results show that yields of off-gas, LPG, and coke increased with the increase of reaction temperature at the same WHSV, but yield of light oil decreased with the increase of reaction temperature at the same WHSV.

Table 3 Effect of reaction temperature and WHSV on the yields (%) of reaction products formed from Yanhua FCC gasoline [9]

Tempera-ture, °C	WHSV, h^{-1}	Off-gas	LPG	Light oil	Coke	Total
	10	0.4	8.7	90.3	0.6	100.0
430	20	0.3	7.6	91.6	0.5	100.0
	30	0.2	7.0	92.4	0.4	100.0
	10	0.5	10.1	88.6	0.8	100.0
450	20	0.4	8.9	90.0	0.7	100.0
	30	0.3	8.3	90.8	0.6	100.0
	10	0.6	12.1	86.4	0.9	100.0
470	20	0.5	9.5	89.2	0.8	100.0
	30	0.4	8.6	90.3	0.7	100.0

Note: Catalyst to oil and water to oil are 6 and 0.05, respectively.

Table 4 indicates the relationships between reaction temperature, WHSV and the yields of light oil. When reaction temperature increased at the same WHSV values, catalytically active energy content of the system increased. This means that the condensation and the isomerization reactions became more intensive, thus the yield of olefins decreased with the increase of reaction temperature at the same WHSV. The yields of aromatic and isoparaffin hydrocarbons, however, increased with the increase of reaction temperature at the same WHSV.

On the other hand, the yields of olefin and aromatic compounds decreased with the increase of WHSV, however, the yield of i-paraffin hydrocarbons increased with the increase of WHSV at the same reaction temperature. These phenomena can be explained as follows: contact time of gasoline and catalyst decreased with the increase of WHSV and gasoline had no more time to react with the catalyst.

Table 4 Effect of reaction temperature and WHSV on the yields (%) of light oil components from Yanhua gasoline[9]

Temperature, °C	WHSV, h^{-1}	n-Paraffins	i-Paraffins	c-Paraffins	Olefins	Aromatics
	10	3.40	25.15	6.03	29.18	36.24
430	20	3.45	26.21	5.83	28.82	35.69
	30	3.39	27.78	7.92	27.45	33.46
	10	3.48	25.46	6.14	28.17	36.75
450	20	3.54	26.45	6.04	27.69	36.28
	30	3.49	27.98	6.42	26.68	35.43
	10	4.05	31.91	6.23	17.62	40.19
470	20	4.12	32.04	7.87	16.47	39.50
	30	4.09	33.15	8.65	15.45	38.66

Table 5 shows the relations between reaction temperature, WHSV and the yields of LPG production from Yanhua FCC gasoline. When WHSV increased at the same reaction temperature, the isomerization and the crack reaction probabilities increased. The experimental results proved the above assumption, because the yields of propylene and i-butane increased, but the yields of n-butane, 2-butylene and 1-butylene decreased with the increase of WHSV at the same reaction temperature. On the other hand, when reaction temperature increased at the same WHSV, the intensity of crack reactions could be increased, while the probability of isomerization reactions was decreased. Consequently, as it was observed, the yield of propylene increased while the yield of i-butane decreased with the increase of reaction temperature at the same WHSV values.

Table 5 Effect of reaction temperature and WHSV on the yields of LPG production from Yanhua FCC gasoline (%, m/m)[9]

Temperature, °C	WHSV, h^{-1}	propane	propylene	i-butane	n-butane	2-butene	1-butene	i-butylene
	10	1.5	43.6	10.1	2.4	14.5	6.7	21.2
430	20	1.5	45.7	11.7	2.1	13.4	5.8	19.8
	30	1.4	46.1	12.2	1.7	12.7	4.9	21.0
	10	2.0	48.4	8.5	1.7	13.7	5.8	19.9
450	20	1.8	49.7	9.1	1.5	12.4	5.1	20.4
	30	1.6	50.4	10.6	1.0	11.5	4.8	20.1
	10	1.4	52.4	4.4	1.4	13.4	6.2	20.8
470	20	1.5	53.1	6.7	0.8	12.5	5.4	20.0
	30	1.5	54.0	8.6	0.5	11.1	4.9	19.4

Note: Catalyst to oil and water to oil are 6 and 0.05, respectively.

Table 6 indicates the relationship between reaction temperature, WHSV, and the yields of aromatics and propylene from Yanhua FCC gasoline. When WHSV increased at the same reaction temperature, the probability of isomerization and crack reactions simultaneously decreased. The experimental results proved the assumption that the catalyst had not much time to contact with gasoline, thus the yields of aromatics, propylene, and aromatics + propylene decreased with the increase of WHSV at the same reaction temperature. On the other hand, when temperature increased at the same WHSV, isomerization and crack reactions could be occurred. The experimental results proved that the catalytically active energy content of the system increased, thus isomerization and crack reactions occurred, therefore the yields of aromatics, propylene, and aromatics + propylene increased with the increase of reaction temperature at the same WHSV.

Table 6 Effect of reaction temperature and WHSV on the yield (%) of aromatics and propylene from Yanhua FCC gasoline (%, m/m)[9]

Temperature, °C	WHSV, h^{-1}	Aromatics	Propylene	Aromatics+ propylene
	10	36.1	3.79	39.89
430	20	35.7	3.47	39.17
	30	33.4	3.23	36.63
	10	36.7	4.89	41.59
450	20	36.3	4.42	40.72
	30	35.4	4.18	39.58
	10	40.1	6.34	46.44
470	20	39.5	5.04	44.54
	30	38.6	4.64	43.24

Note: Catalyst to oil and water to oil are 6 and 0.05, respectively.

Effects of reaction temperature and WHSV on fraction of Yanhua FCC gasoline (boiling point < 90 °C)

Table 7 shows the relationships between reaction temperature, WHSV and the yields of fraction formed from Yanhua FCC gasoline. The trends obtained using the selected fraction of Yanhua gasoline (b.p.<90 °C) were the same as the trends observed at Yanhua FCC gasoline. When WHSV increased, gasoline had less time to contact with the catalyst, so yields of LPG and coke decreased with the increase of WHSV at the same reaction temperature. The yield of light oil increased with the increase of WHSV at the same reaction temperature. When reaction temperature increased the catalytically active energy content also increased. It means that more crack reactions took place. The experimental results showed that yields of LPG and coke increased with the increase of reaction temperature at the same WHSV, while the yield of light oil decreased with the increase of reaction temperature at the same WHSV.

Table 7 Effect of reaction temperature and WHSV on the yields (%) of products from a Yanhua FCC gasoline fraction (b.p.<90 °C)

Tempera-ture, °C	WHSV, h^{-1}	Off-gas	LPG	Light oil	Coke	total
	10	0.1	5.5	93.7	0.7	100.0
430	20	0.1	5.1	93.9	0.9	100.0
	30	0.1	4.6	94.1	1.2	100.0
	10	0.1	6.7	92.4	0.8	100.0
450	20	0.2	6.0	92.8	1.0	100.0
	30	0.2	5.4	93.7	1.3	100.0
	10	0.5	9.4	89.2	0.9	100.0
470	20	0.5	8.0	90.4	1.1	100.0
	30	0.6	6.5	91.5	1.4	100.0

Note: catalyst to oil and water to oil are 6 and 0.05, respectively.

Table 8 indicates the relationships between reaction temperature, WHSV and the yields of products from a selected fraction (<90°C) of Yanhua FCC gasoline. When reaction temperature increased at the same WHSV, the catalytically active energy content increased. This means that the probability of the condensation and the isomerization reactions increased, therefore the yields of olefins and i-paraffins decreased with the increase of reaction temperature at the same WHSV, however, the yields of aromatics increased with the increase of reaction temperature at the same WHSV.

On the other hand, yields of aromatics decreased with the increase of WHSV at the same reaction temperature, but yields of i-paraffins and olefins increased with the increase of WHSV at the same reaction temperature. These phenomena are explained as follows: contact time of gasoline and catalyst decreased with the increase of WHSV and gasoline had not much time to react with the catalyst.

Table 9 shows the relationships between reaction temperature, WHSV, and yields of LPG production of a selected fraction (b.p. <90 °C) of Yanhua FCC gasoline. When WHSV increased at the same reaction temperature, the crack reactions became more frequent. The experimental results proved the assumption, that the yields of propane, i-butane, n-butane, 2-butylene, and 1-butylene were increased with the increase of WHSV at the same reaction temperature, but the yields of propylene and i-butylene decreased with the increase of WHSV at the same reaction temperature.

On the other hand, when reaction temperature increased at the same WHSV, the probability of crack and isomerization reactions decreased. For example, the yields of propylene and propane increased with the increase of reaction temperature at the same WHSV.

Table 8 Effect of reaction temperature and WHSV on the yield (%) of light oil components from a fraction (b.p.<90 °C) of Yanghua gasoline

Temperature, °C	WHSV, h^{-1}	n-Paraffins	i-Paraffins	c-Paraffins	Olefins	Aromatics
	10	4.76	35.31	8.49	36.12	15.32
430	20	4.81	35.74	7.98	36.43	15.04
	30	4.79	36.21	6.98	37.35	14.67
	10	4.87	35.64	9.81	31.84	17.84
450	20	4.80	35.98	8.64	33.33	17.25
	30	4.86	36.54	7.18	35.64	15.78
	10	4.98	37.78	8.70	28.90	19.64
470	20	5.12	38.17	7.66	29.64	19.41
	30	5.07	39.76	5.90	30.81	18.46

Note: Catalyst to oil and water to oil are 6 and 0.05, respectively.

Table 10 indicates the relationships between reaction temperature, WHSV, and the yields of aromatic hydrocarbons and propylene from the selected fraction (b.p.<90 °C) of Yanhua FCC gasoline. The trends obtained were the same as the trends observed at unfractionated Yanhua FCC gasoline. When WHSV increased at the same reaction temperature, the isomerization and the crack reactions probability decreased. The experimental results proved the assumption that the catalyst had no more time to contact with gasoline, thus the yields of aromatics, propylene and aromatics + propylene decreased with the increase of WHSV at the same reaction temperature. When reaction temperature increased at the same WHSV, isomerization and crack reactions were intensified. The experimental results proved that catalytically active energy content, the isomerization and the crack reactions, the yields of aromatics, propylene, and aromatics+ propylene increased with the increase of reaction temperature at the same WHSV.

Table 9 Effect of reaction temperature and WHSV on the yields of LPG products from the fraction of Yanhua FCC gasoline (b.p. < 90 °C) (%, m/m)[9]

Temperature, °C	WHSV, h^{-1}	propane	propene	i-butane	n-butane	2-butene	1- butene	i- butene
	10	2.3	44.7	8.6	2.1	13.8	5.2	23.3
430	20	2.7	40.6	10.4	2.9	14.1	5.4	23.9
	30	3.1	38.6	13.7	3.6	14.7	5.8	20.5
	10	2.6	48.2	8.1	1.8	12.7	4.8	21.8
450	20	2.6	44.2	9.6	3.4	13.4	5.1	21.7
	30	3.2	39.8	12.4	4.2	13.9	5.6	20.9
	10	2.8	52.4	7.7	1.8	11.5	4.8	19
470	20	3.1	51.1	8.4	2.4	11.9	5.0	18.1
	30	3.4	50.3	9.1	3.2	12.4	5.4	16.2

Note: catalyst to oil and water to oil are 6 and 0.05, respectively.

Table 10 Effect of reaction temperature and WHSV on the yields of aromatics and propylene from a fraction of Yanhua FCC gasoline (b.p. <90°C) (%, m/m)

Temperature, °C	WHSV, h^{-1}	Aromatics	Propylene	Aromatics+ propylene
	10	15.3	0.84	16.14
430	20	15.0	0.77	15.77
	30	14.6	0.67	15.27
	10	17.9	1.20	19.1
450	20	17.2	1.03	18.23
	30	15.7	0.85	16.55
	10	19.6	1.84	21.44
470	20	19.4	1.55	20.95
	30	18.5	1.20	19.7

Note: Catalyst to oil and water to oil are 6 and 0.05, respectively.

Conclusion

Aromatization reactions of Yanhua FCC gasoline and a fraction of Yanhua FCC gasoline (b.p.<90 °C) have been studied by using LBO-A as catalyst in a confined fluidized bed reactor. The experimental results are shown as follows:

(1) Yields of off-gas, LPG, and coke decreased with the increase of WHSV at the same reaction temperature, but yields of light oil increased with the increase of WHSV at the same reaction temperature; yields of off-gas, LPG, and coke increased with the increase of reaction temperature at the same WHSV, but yields of light oil decreased with the increase of reaction temperature at the same WHSV.

(2) Yields of olefin and i-paraffin hydrocarbons decreased with the increase of reaction temperature at the same WHSV, but yields of aromatics increased with the increase of reaction temperature at the same WHSV; yields of olefins and aromatics decreased with the increase of WHSV at the same reaction temperature, but yields of i-paraffins increased with the increase of WHSV at the same reaction temperature.

(3) Yields of propylene and i-butane increased with the increase of WHSV at the same reaction temperature, but yields of n-butane, 2-butylene and 1-butylene decreased with the increase of WHSV at the same reaction temperature; yields of propylene increased with the increase of reaction temperature at the same WHSV, while yields of i-butane decreased with the increase of reaction temperature at the same WHSV.

(4) Yields of aromatics, propylene and aromatics plus propylene decreased with the increase of WHSV at the same reaction temperature; yields of aromatics, propylene and aromatics + propylene increased with the increase of reaction temperature at the same WHSV.

(5) Reaction results obtained with a selected fraction (b.p. <90 °C) of Yanhua FCC gasoline showed the same trend and gave almost the same results as the Yanhua FCC gasoline.

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Received: 21.08.2012.
Accepted: 23.08.2012.