

Study on the Technology of Moderate Hydrocracking of Straight Run Diesel to Produce More Ethylene Cracking Feedstock

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Abstract. By optimizing the composition of the catalyst support material, using amorphous silica alumina with high mesoporous content as the main support and modified beta molecular sieve with excellent aromatics ring opening selectivity as the acidic component, a hydrocracking catalyst suitable for producing high quality ethylene cracking feedstock at low cost was developed. The catalyst has high selectivity for PAHs cracking, while the alkanes are retained in the diesel fraction, which can achieve the purpose of producing more ethylene cracking feedstocks with low BMCI value under medium and low pressure conditions, and provide strong technical support for refining and chemical transformation.

Keywords: Straight run diesel, Mild hydrocracking, Catalyst, Ethylene cracking feedstock, Process research.

1 Introduction

Ethylene is one of the important chemical raw materials in petrochemical industry. At present, China is the second largest ethylene producer in the world after the United States [1-2]. In 2020, the ethylene production capacity will be 34.91 million tons, with an annual growth rate of 20.9%, and the propylene production capacity will be 43.99 million tons, with an annual growth rate of 20.6%. It is expected that the annual growth rate of 6-8% will be maintained in the next few years, but there is still a large gap in consumption. With the long-term stable growth of market demand and production capacity, refining and chemical industry needs to broaden the source of ethylene cracking raw materials and increase ethylene production through multiple routes.

With the decline of oil demand, China's diesel consumption has basically reached the peak, and the diesel consumption will decrease year by year. In 2020, the total apparent consumption of diesel will be 140.48 million tons, a year-on-year decrease of 3.7%. It is estimated that by 2025, the consumption ratio of diesel to gasoline will drop to 0.75. Therefore, reducing the ratio of diesel to gasoline, reducing oil consumption and increasing chemical consumption have become the development trend. Straight run diesel is the largest diesel component in the refinery, accounting for about 50wt% of the diesel pool composition. With the urgent demand of refinery production structure adjustment, transformation and upgrading, the reasonable and efficient processing and utilization of straight run diesel has become one of the focuses of refineries.

In order to increase the supply of ethylene raw materials, accelerate the pace of enterprise transformation and upgrading, and improve the market competitiveness, a petrochemical company of PetroChina plans to build a new ethylene plant, and at the same time use the existing diesel hydrofining unit for transformation, so as to realize the conversion of diesel into ethylene raw materials with low cost and high efficiency. In order to improve the economic benefit of refining and chemical enterprises, Petrochina Daqing Petrochemical Research Center has carried out the technology development of producing high quality ethylene cracking feedstock with low cost by selective hydrogenation ring opening cracking of straight run diesel oil.

The focus of this study is to develop a hydrocracking catalyst suitable for producing high quality ethylene cracking feedstock at low cost through carrier modification technology, selection and optimization of active components. To provide technical support for the refining transformation of the enterprise, the performance of straight run diesel hydrocracking to produce more ethylene cracking

feedstock was studied under the process conditions of the existing diesel hydrofining unit in a petrochemical company of PetroChina.

2 Test Part

2.1 Preparation of catalyst

A certain amount of modified mesoporous beta molecular sieve, mesoporous alumina, mesoporous amorphous silica alumina and Sesbania powder were mixed, then the mixed solution of concentrated nitric acid, citric acid and water was added, extruded into a 1.3mm cylinder, dried at 100 °C and calcined at 540 °C for 4H, the carrier was prepared. Then, ammonium metatungstate and nickel nitrate were prepared into a metal co leaching solution according to a certain proportion, and the support was co impregnated by saturated impregnation. After impregnation, the catalyst was prepared by drying at 120 °C for 4 h and calcining at 500 °C for 4 h. According to the specific requirements, broken or cut to the required particle size or length, hydrogenation reaction can be carried out after vulcanization.

2.2 Physical and chemical properties analysis of the carrier and catalyst

The specific surface area, bulk density, composition and strength of the support and catalyst were analyzed. The results are shown in Table 1.

Table 1. Physicochemical properties of carrier and catalyst

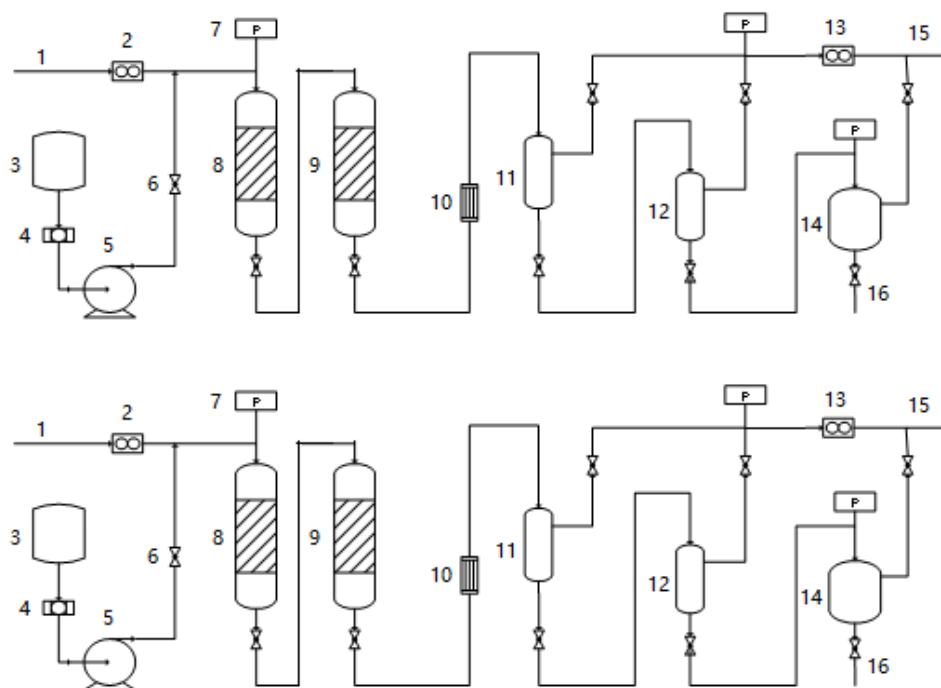
Items		Value
carrier	specific surface area, m ² /g	426
	bulk density, g/mL	0.48
	Strength, N/cm	205
catalyst	WO ₃ +NiO, wt%	28.2
	bulk density, g/mL	0.87
	Strength, N/cm	176

By optimizing the composition of catalyst carrier materials, the amorphous aluminum silicon and alumina with high mesoporous content as the main carriers, the modified beta zeolite with excellent aromatics ring opening selectivity as acid component and W-Ni as active metal component, a diesel hydrocracking catalyst was successfully prepared, which was suitable for the largest amount of ethylene cracking feedstock with low BMCI value. In the process of straight run diesel hydroconversion, the internal diffusion performance of PAHs in molecular sieves has a very important impact on the activity of the catalyst. Compared with conventional amorphous silica alumina, amorphous silica alumina with high mesoporous content has more mesoporous structure, which is conducive to improving the diffusion rate and ring opening cracking ability of PAHs and cycloalkanes.

2.3 Performance evaluation of catalyst

2.3.1 Evaluation device

The evaluation was carried out in "PetroChina hydrogenation catalyst and process engineering test base" of Daqing Chemical Research Center. The evaluation device is 200ml fixed bed hydrogenation test device, as shown in Fig. 1 and Fig. 2. The catalytic performance of the developed catalyst was evaluated by using the process of raw material and hydrogen passing through at one time.



1.Hydrogen 2.Hydrogen flowmeter 3.Stock tank 4.Filter 5.Feed pump 6.Ball check 7.Pressure gauge 8.First reactor 9.Second reactor 10.Cooler 11.High pressure separator 12.Low pressure separator 13.Tail gas flowmeter 14.Product tank 15.Tail gas 16.Sampling port

Figure 1. Flow diagram of 200ml hydrogenation evaluation unit

2.3.2 Analysis method

The oil analysis items and methods used in the test are shown in Table 2.

Table 2. Analysis items and analysis methods.

Items	analysis method
density	GB/T 1884
Sulfur content of raw material	GB/T 17040
Nitrogen content of raw materials	ASTM D4629
Sulfur content of product	SH/T 0689
Nitrogen content of product	ASTM D4629
Distillation range	ASTM D86
True boiling point distillation	ASTM D2892
BMCI value	GB/T 6536
Hydrocarbon composition	SH/T 0606

2.3.3 Raw materials of evaluation

The hydrogen used in the test is industrial hydrogen from the Chemical Plant of A Petrochemical Company, and its composition is shown in Table 3.

The two diesel feedstocks used in the test are intermediate based straight run diesel from a refinery of a petrochemical company of PetroChina, and their properties are shown in Table 4.

Table 3. Analysis of hydrogen composition for the test

composition	H ₂	CH ₄	C ₂ H ₆	CO	N ₂	analytical method
Content, φ%	96.300	1.909	0.002	0.002	1.787	gas chromatographic method

Table 4. Properties of two diesel feedstocks

Items	Intermediate based straight run diesel	Intermediate based straight run diesel
	1#	2#
Density (20°C) , g/cm ³	0.8348	0.8392
sulphur content, μg/g	5330	2673
nitrogen content, μg/g	77	57
Distillation range, °C	HK	171
	10%	202
	30%	237
	50%	273
	70%	308
	90%	345
	KK	367
BMCI value	29.2	27.1
	Alkanes	44.5
	Cycloparaffins	33.7
Hydrocarbon composition, wt%	Aromatics	21.0
	Monocyclic	14.7
	Bicyclic	5.7
	Tricyclic	0.6

3 Evaluation Results and Discussion

3.1 Properties and characteristics of middle base straight run diesel oil

Alkanes in ethylene cracking feedstock can be directly cracked to produce ethylene and other low-carbon olefin products, while cycloalkanes and aromatics are more prone to condense to produce heavy aromatics or even coking. Therefore, the yield of ethylene and other low-carbon olefins in the products is determined by the content of alkanes, while the content of cycloalkanes and aromatics will affect the operation cycle of cracking unit^[3,4]. Generally, correlation index (BMCI) is used to characterize the aromaticity of hydrocarbons. The higher the value is, the higher the aromaticity is and the worse the cracking performance is.

From table 4, it can be seen that the intermediate base straight run diesel has the characteristics of low density, low nitrogen content and high naphthenic hydrocarbon and aromatics content; from the analysis data of hydrocarbon composition, it can be seen that the chain alkane content of the two kinds of intermediate base direct run diesel is about 45wt%, the cycloalkanes content is over 33wt%, the aromatics content is over 21wt%, and the polycyclic aromatic hydrocarbons content is over 6.0wt%; the BMCI values are 29.2 and 27.1 respectively. Compared with high quality ethylene cracking feedstock, straight run diesel has lower alkane content, higher aromatics content and higher BMCI, so it is not suitable to be used as ethylene cracking feedstock directly.

If intermediate based straight run diesel is used to produce ethylene cracking feedstock, it is necessary to enrich naphthenic and aromatic hydrocarbons into naphtha fraction through selective ring opening cracking and other reactions, and retain alkanes in diesel products, so as to improve the content of alkanes in diesel products, reduce the content of aromatic hydrocarbons and obtain high-quality ethylene cracking feedstock.

3.2 Performance evaluation of selective hydrocracking of straight run diesel

In this study, using 1 # and 2 # intermediate based straight run diesel as raw materials respectively, the performance of selective hydrotreating opening cracking of straight run diesel oil was evaluated by using mature hydrotreating catalyst and developed diesel hydrocracking catalyst under the condition of unit production plan.

3.2.1 Evaluation results of 1# intermediate based straight run diesel

Table 5 shows the evaluation results of 1 # intermediate based straight run diesel.

Table 5. Evaluation results of 1 # intermediate based direct diesel in a Petrochemical Company

Items	Raw material(1 # intermediate based straight run diesel)		Product			
Process conditions						
Pressure, MPa			6.7			
Hydrogen-oil ratio, (V/V)			250: 1			
Temperature(Refining / cracking), °C	-		350/367			
LHSV of cracking, h ⁻¹			3.0			
Liquid yield/wt%	-		98.3			
Fractions at different temperatures, °C	-		Whole fraction	<155	155-235	>235
Yield of different fractions, wt%	-		-	28.8	28.5	42.7
Density, (g/cm ³) (20°C)	0.8348	0.7970	0.7198	0.8026	0.8153	
sulfur content, (μg/g)	5330	6.8	2.4	5.7	9.1	

nitrogen content, ($\mu\text{g/g}$)	77	<1	<1	<1	<1
Distillation range, $^{\circ}\text{C}$					
HK	194	57.3	39.5	163.8	245.5
10%	229	147.2	66.3	182.2	257.8
30%	248	216.5	85.2	193.1	263.6
50%	269	243.4	102.0	202.0	274.0
70%	296	273.0	117.4	209.6	291.9
90%	342	328.9	136.4	218.9	329.2
KK	372	358.8	157.9	227.8	357.8
BMCI value	29.2	-	16.0	27.5	18.3
Hydrocarbon composition, wt%					
Alkanes	44.5	-	-	39.6	59.2
Cycloparaffins	33.7	-	-	42.8	31.1
Aromatics	21.8	-	-	17.6	9.7
Monocyclic	15.0	-	-	17.1	8.3
Bicyclic	6.3	-	-	0.4	1.3
Tricyclic	0.5	-	-	0.1	0.1
Naphtha + diesel yield, wt%	-	71.5			

The results showed that the yield of ethylene cracking feedstock (naphtha + diesel) could reach 71.5wt% under the conditions of pressure of 6.7mpa, refining/cracking reaction temperature of (350/367) $^{\circ}\text{C}$, hydrogen oil ratio of 250:1 and cracking space velocity of 3.0h⁻¹, and the BMCI values of naphtha and diesel were 16.0 and 18.3 respectively, which could be used as ethylene cracking feedstock. However, the BMCI value of kerosene is 27.5, the aromatics content of kerosene is still very high, which is not suitable for ethylene cracking and can be used as blending component of low pour point diesel.

3.2.2 Evaluation results of 2# intermediate based straight run diesel

Table 6 shows the evaluation results of 2 # intermediate based straight run diesel.

Table 6. Evaluation results of 2 # intermediate based direct diesel in a Petrochemical Company

Items	Raw material(2 # intermediate based straight run diesel)	Product
Process conditions		

Pressure, MPa				6.4	
Hydrogen-oil ratio, (V/V)				350:1	
Temperature (Refining/ cracking), °C	-			345/362	
LHSV of cracking, h ⁻¹				1.84	
Liquid yield/wt%	-			98.8	
Fractions at different temperatures, °C	-	Whole fraction	<155	155-235	>235
Yield of different fractions, wt%	-	-	48.73	25.64	24.96
Density, (g/cm ³)(20°C)	0.8392	0.7473	0.7166	0.7880	0.8107
sulfur content, (µg/g)	2673	4.3	1.6	3.2	6.7
nitrogen content, (µg/g)	57	<1	<1	<1	<1
Distillation range, °C					
HK	171	29.0	33.3	163.2	237.0
10%	202	82.5	63.3	173.6	257.1
30%	237	131.1	81.7	179.7	266.8
50%	273	177.1	99.7	186.9	282.3
70%	308	238.0	116.9	197.0	304.1
90%	345	340.7	137.9	213.5	337.4
KK	367	362.3	154.7	228.3	361.9
BMCI value	27.1	-	15.0	22.6	15.2
Hydrocarbon composition, wt%					
Alkanes	54.4	-	-	43.9	64.1
Cycloparaffins	33.6	-	-	39.1	26.1
Aromatics	21.0	-	-	17.0	9.8
Monocyclic	14.7	-	-	16.4	8.1
Bicyclic	5.7	-	-	0.5	1.5
Tricyclic	0.6	-	-	0.1	0.2
Naphtha + diesel yield, wt%	-			73.7	

The results showed that the yield of ethylene cracking feedstock (naphtha+diesel) could reach 73.7wt% under the conditions of pressure of 6.4mpa, refining/cracking reaction temperature of (345/362) °C, hydrogen oil ratio of 350:1 and cracking space velocity of 1.84h⁻¹, and the BMCI values of naphtha and diesel were 15.0 and 15.2 respectively, which could be used as high quality ethylene cracking feedstock with low BMCI value. However, the BMCI value of kerosene is 22.6, the aromatics content of kerosene is still very high, which is not suitable for ethylene cracking and can be used as blending component of low pour point diesel.

4 Conclusions

(1) A diesel oil hydrocracking catalyst was successfully prepared by using amorphous silica alumina and alumina with high mesoporous content as main carriers, modified beta molecular sieve with excellent aromatics ring opening selectivity as acidic component and W-Ni as active metal component.

(2) Under the conditions of low pressure, high space velocity and low hydrogen to oil ratio (pressure 6.7mpa, cracking space velocity 3.0h⁻¹, hydrogen/oil ratio 250:1), the yield of ethylene cracking feedstock can reach 71.5wt%, and the BMCI values of naphtha and diesel are 16.0 and 18.3 respectively.

(3) Under the conditions of pressure 6.4Mpa, cracking space velocity 1.84h⁻¹ and hydrogen oil ratio 350:1, the yield of ethylene cracking feedstock (naphtha + tail oil) can reach 73.7 wt%, and the BMCI

values of naphtha and tail oil are 15.0 and 15.2 respectively, which can be used as high-quality ethylene cracking feedstock with low BMCI value.

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