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Co-feeding with DME: An effective way to enhance gasoline production via low temperature aromatization of LPG

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Abstract

The aromatization of light alkenes in liquefied petroleum gas (LPG) with and without dimethyl ether (DME) addition in the feed was investigated on a modified ZSM-5 catalyst. The results showed that under the given reaction conditions the selectivity of alkenes to high-octane gasoline blending components was markedly enhanced and the formation of propane and butanes was greatly suppressed with the addition of DME. It was also found that the distribution of C_{5+} components was changed a lot with DME addition into the LPG feed. The formation of branched hydrocarbons (mainly C_6–C_8 i-paraffin) and multi-methyl substituted aromatics, which are high octane number gasoline blending components, was promoted significantly, while the content of n-paraffins and olefins in C_{5+} components was decreased obviously, indicating that in addition to the oligomerization, cracking, hydrogen-transfer and dehydrogenation-cyclization of alkenes, the methylation of the formed aromatics and olefins intermediates also plays an important role in determining the product distribution due to the high reactivity of surface methoxy groups formed by DME. And this process, in combination with the syngas-to-methanol/DME technology, provides an alternative way to the production of high-octane gasoline from coal, natural gas or renewable raw materials.

Key words

aromatization; gasoline; alkene; butene; dimethyl ether; co-feeding; ZSM-5

1. Introduction

In recent years, driven mainly by the changes of market demand, much attention has been focused on developing green and flexible processes/technologies on catalytic transformation of light hydrocarbons to value-added products, such as liquefied petroleum gas (LPG) aromatization [1,2], catalytic cracking of C_{4+} alkenes [3], metathesis of 2-butene and ethene [4], dehydrogenation of propane and butanes [5], etc.

As far as the LPG aromatization process is concerned, owing to the inertness nature of light alkanes, it requires a relatively high reaction temperature, which inevitably generates a considerable amount of dry gas [6], mainly consisting of methane and ethane. Alkenes are more active than alkanes with the same carbon number and can be transformed into aromatics at a relatively lower reaction temperature. Recently, based on a modified ZSM-5 zeolite catalyst (DL0810), a novel process for high-octane gasoline blending components production via alkenes or alkenes-rich light hydrocarbons low-temperature aromatization has been developed by Dalian Institute of Chemical Physics (DICP), Chinese Academy of Sciences (CAS) and commercialized with a capacity of 200000 tons per year in 2011. The industrial running results showed that the content of dry gas in the products can be controlled to less than 1.5 wt%, demonstrating that it is a green, flexible and economic route for LPG transformation to high-octane gasoline blending components.

During the practice of the above-mentioned work, we have noted that the product distribution of LPG aromatization also depends on the reaction conditions and raw materials. In the present work, we report a novel feed mode of LPG aromatization, which is co-feeding with dimethyl ether (DME). We have found that co-feeding with DME is an effective way to enhance the selectivity of alkenes to high-octane gasoline blending components via low-temperature aromatization of LPG. And this process, in combination with the syngas-to-methanol/DME technology, provides an alternative way to the production of high-octane gasoline from coal, natural gas or renewable raws.

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2. Experimental

Transformation of LPG (DL-Petro, CNPC) and/or DME to gasoline was carried out in a continuous stainless steel reactor (16 mm diameter) with a thermocouple in the center of the catalyst bed. The catalyst, based on the modified ZSM-5 developed by DICP, was activated at 520 °C for 1 h under a nitrogen flow before starting a reaction run. Then, the feed was pumped and passed through the reactor under certain reaction conditions. Unless otherwise noted, the reaction conditions are the same as those of typical industrial operations: 1.0 MPa, 330−370 °C (inlet and outlet temperature, respectively) and a total hydrocarbon WHSV of 0.66 h^{-1} (the conversion coefficient of DME to hydrocarbon is 60.87%).

The reaction products, including the gaseous products, the liquid products and the unreacted DME, were analysed by Varian 3800 gas chromatograph equipped with a FID and a PONA column, the content of H_2, COx and CH_4 in the gaseous products was also analysed by Shimadzu GC-8A equipped with a TCD and a TDX01 column, and all the products distribution, except for H_2O, was normalized to 100%.

The reaction parameters such as conversion (Conv), selectivity (Sel) and equivalent concentration (Conc) of alkenes in the hydrocarbon (CH_x) feed are defined as follows.

$$\text{Conv} = \frac{\text{R\% in the feed} - \text{R\% in the products}}{\text{R\% in the feed}} \times 100\%$$

where, R (reactant) = C_4H_8 or DME

$$\text{Sel}_{(CxHy)} = \frac{C_xH_y(\%) \text{ in the products}}{C_iH_j(\%) \text{ in the products}} \times 100\%$$

where, the CO_x was regarded as C_1H_0, H_2 as C_0H_2, and H_2O is not included, if there is, and x, y, i and j belong to natural number.

Equivalent concentration of alkenes in the CH_x feed = (DME wt% in the feed × 60.87% + LPG wt% in the feed × 44.54%)/(DME wt% in the feed × 60.87% + LPG wt% in the feed)

where, 60.87% comes from: [molar mass of $(CH_2)_2$/molar mass of DME (C_2H_6O)]×100%, and the concentration of alkenes in LPG is 44.54 wt% (Table 1).

3. Results and discussion

3.1. Effect of DME addition on the total product distribution of LPG transformation

Table 1 lists the composition of the remnant C_4 fraction LPG after methyl tert-butyl ether (MTBE) production. The weight percentage of C4 alkenes in LPG used in this work is 44.54 wt%, and the other is mainly composed of i-butane and n-butane. And Table 2 lists the equivalent weight percent of H_2O, CH_2 in the feed and equivalent concentration of alkenes in CH_x feed with different DME wt%. Because DME transformation to hydrocarbons on acidic zeolite catalyst goes through light alkenes intermediates, mainly ethene, propene and butenes, the DME, with molecular formula of CH_3OCH_3, is considered as "60.87 wt% alkenes or CH_2 + 39.13 wt% H_2O". And the equivalent concentration of alkenes in the hydrocarbon (CHx) feed increased from 44.54% to 65.50% when the DME weight percentage in the feed increased from 0 to 50%.

Table 1. Composition of the remnant C_4 fraction after MTBE production

Component	Content (wt%)
⩽C_3(mainly propane)	1.28
n-Butane	11.93
i-Butane	41.82
1-Butene	14.91
$trans$-2-Butene	17.72
cis-2-Butene	11.91
⩾C_5	0.43
Total C_4 alkenes	44.54

Table 2. Equivalent weight percent of H_2O and CH_2 in the feed and equivalent concentration of alkenes in CH_x feed with different DME (wt%)

No.	Items	Content (wt%)					
(1)	DME (wt%) in the feed	0	18	30	40	50	100
(2)	LPG (wt%) in the feed	100	82	70	60	50	0
(3)	E(H_2O) in DME fraction (wt%)	0	7.04	11.74	15.65	19.57	39.13
(4)	E(CH_2) in DME fraction (wt%)	0	10.96	18.26	24.35	30.43	60.87
(5)	E(CH_2)/alkenes in LPG fraction (wt%)	44.54	36.52	31.18	26.72	22.27	0
(6)	Total E(CH_2) in the feed (wt%)	44.54	47.48	49.44	51.07	52.70	60.87
(7)	Total E(CHx) in the feed (wt%)	100.00	92.96	88.26	84.35	80.43	60.87
(8)	Equivalent concentration of alkenes in CHx feed* (wt%)	44.54	51.08	56.01	60.55	65.52	100.00

(6) = (4)+(5); (7) = (2)+(4); (8) = [(6)/(7)]×100%; *H_2O is not included; E: the abbreviation of equivalent

Transformation of LPG and/or DME on DL0810 aromatization catalyst was carried out under 1.0 MPa, 330−370 °C (inlet and outlet temperature, respectively) and a total hydrocarbon WHSV of 0.66 h^{-1}(the conversion coefficient of DME to hydrocarbon is 60.87%, as mentioned above). Under the above reaction conditions, due to the high reactivity of DME and C_4 alkenes, their conversion on the catalyst was in the range of 97.83% to 100%, and the DME conversion