Selective Hydroconversion of Diesel Boiling Range Heavy-Aromatics for Xylene-rich BTX Production

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Increasing global environmental concerns limit the use of heavy aromatic products in fuel pools. Hence, there has been a strong demand for upgrading heavy aromatics of diesel boiling range into high value products [1-2]. The C_{10}^+ heavy aromatics from *p*-xylene plants is a representative by-products containing alkyl benzenes, naphtheno benzenes, and polycyclic aromatics such as naphthalene, alkyl-naphthalenes, methylbiphenyl, and dimethyl-biphenyl etc.

We postulated a two-step catalytic process to convert aromatic-rich by-products into highvalue BTX [3]. To achieve high per-pass yield of BTX from aromatic-rich fractions, it is important to convert the 2- and 3-ring into 1-ring products in high aromatics selectivity in the pretreatment reaction followed by selective hydrocracking (HYC) of 1-ring aromatics into BTX. In our previous study, we showed that naphthalene can be converted to tetralin by selective hydrogenation over Mo_2C/γ -Al₂O₃ the catalysts [3] and high yield of BTX can be achieved from selective hydrocracking of tetralin over metal-supported zeolites [4].

In this study, the catalytic hyroconversion of C_{10}^{+} aromatics from a *p*-xylene plant was studied in a fixed bed down-flow microreactor system operated under the total pressure of 40-50 MPa at 375-450 °C.

The results of hydrocracking of C_{10}^+ aromatics obtained from 1-step (direct hydrocracking) and 2-step hyroconversion at 425 °C are compared in **Table 1**. Both catalytic processes showed very high level of conversion. Direct hydrocracking resulted in the production of a large amount of C_{11}^+ aromatics as well as alkylbenzenes as a sideproducts compared with the results from a two-step catalytic process. The final BTX yield from the two-step catalytic process was much higher than that from the direct hydrocracking due to the better control of exothermic heat and chemical equilibrium involved in the hydroconversion process. Unlike the results from model hydrocracking study with tetralin, xylene content was the highest among BTX and large amount of trimethylbenzenes were co-produced. These results could be due to the transalkylation between benzene or toluene and tetramethylbenzenes present in the feed of C_{10}^+ aromatics (**Figure 1**).

In overall, the C_{10}^{+} heavy aromatics from *p*xylene plants can be selectively converted to xylene-rich BTX. The C_{10}^{+} heavy aromatics can also be used as a co-feed of other heavy aromatics (such as LCO and PFO) for the purpose of boosting xylene yield via transalkylation.

Table 1. Comparison of results from 1-step and 2-step hydroconversion of C_{10}^{+} aromatics.

	Conv.(%)		Liq. Product distribution, wt%							
			Nonaros.	Benzene	Toluene	Xylene	TMBs	Alkyl benzenes	C ₁₁ ⁺ Aros.	Others
1-step	Naph. Conv.	M-Naph. Conv.	4.4	7.2	18.5	18.4	10.9	13.6	18.4	8.7
	91.1	75.5		BTX Yield		38.3		BTX + T	52.3	
2-step	Tet. Conv.	M-Tet. Conv.	7.9	6.3	23.1	32.7	18.1	6.6	3.9	1.4
	99.1	94.2		BTX Yield		46.1		BTX + T	MBs Yield	59.5



Figure 1. Comparison of BTX distribution obtained from the hydrocracking of (a) tetralin and (b) process C_{10}^+ aromatics, and (c) proposed transalkylation reactions leading to high yield of xylenes.

REFERENCES

- M. Bouchy, S. Peureux-Denys, P. Dufresne and S. Kasztelan, *Ind. Eng. Chem. Res.* 32 (1993) 1592.
- [2] S. Choi, D. W. Kim, *PCT Patents*, WO 2012053853 A2 (2012).
- [3] Y. Choi, J. Lee, J. Shin, S. Lee, D. Kim and J. K. Lee, *Appl. Catal. A*, 492 (2015) 140.
- [4] J. Lee, Y. Choi, J. Shin and J. K. Lee, Catal. Today 265 (2016) 144.