Hydrogenation research on C5 raffinate of C5 distillate in pygas oil

Hsun-yi Huang*[a], Wei-bin Su[a], Cheng-tsung Hong[a], Chang-fa Shiu[b], and Wen-huang Lai[b]

[a] Department of Process Research,CPC Corporation,Taiwan.
[b]Petrochemical Business Division, CPC Corporation,Taiwan.
*Email : 078204@cpc.com.tw

Abstract

In 2013,Taiwan-CPC will produce 720,000 ton ethylene every year in new No. 3 naphtha cracker, causing C5 distillate of pygas oil to increase. For enhancing the C5 distillate output value, Taiwan-CPC launches the consultation with downstream manufacturer by the joint capital to build a factory. It will refine isoprene, piperylene(PIP) and dicyclopentadiene(DCPD) from the C5 distillate of pygas oil. In the isoprene process, it uses extractive distillation to produce isoprene and C5 raffinate. The C5 raffinate includes C5 sateurated and C5 olefin which generally mixes into 92 unleaded gasoline. If the C5 olefin is saturated by hydrogenation process, the product will be used as special solvent for plastic foaming agent. The C5 raffinate hydrogenation tests select 2-methyl-2-butene to represent the iso-pentene, and 2-pentene to represents the n-pentene, and make the diluent with the n-heptane. Hydrogenation experiments are carried on the palladium(Pd) and nickel(Ni) catalyst supported by aluminium oxide. The experiment results show Pd and the high Ni content catalysts have good hydrogenation effect. when reaction temperature is 80℃ and reaction pressure 30kg/cm2, the C5 alkenes conversion rate is 92.4% on 0.3wt% Pd catalyst. If we use 50wt% Ni content catalyst, it may enhance the conversion rate to 99%.

Keywords : hydrogenation, raffinate, conversion rate.

1. Introduction

In recent years, environmental protection consciousness gained ground, enables high ozone depletion potential (ODP) and the global warming potential (GWP) characteristic chemical to eliminate. Hydrogen chloro-fluoro-hydrocarbons (HCFCs) is the commonly used foaming agent, and HCFC-141 compound has high ODP and GWP, which has big impact to the environment[1-4]. in 2007, the Montreal protocol which convenes in the Canadian Montreal 19th time

concluded a treaty and passed the HCFCs foaming agent elimination time interval. The development country must stop production and consummation before 2030 and request China's HCFCs production and consummation to freeze in 2009 and 2010 mean value before 2013. After all, the production and consummation will stop in 2030, therefore we must change foaming agent with the environmental protection chemical.CO2 is one kind of the foaming agent, but it is easy to shrink the product in the manufacture process. The foaming agent of pentane has low ODP and GWP and is available substitutes for the HCFCs. Now, European Union, America and Japan have substituted for the HCFC foaming agent with the pentane in the refrigerator and the heat preservation material. The C5 raffinate of C5 distillate in pygas oil is hydrogenated to pentane which is used as foaming agent and transforms C5 raffinate which is mixed into 92 non-lead gasoline originally into high value solvent.

2. Experiment and result

By way of simulation result of Aspen, C5 faffinate component are listed in table 1.The main composition is 1,3-butadiene, i-pentane, pentene, 2-methylbutene-1 and n-pentane. The saturated hydrocarbon is 36.5wt% and after the hydrogenation the i-pentane is 39.7wt%. We use 2-pentene to represent the linear chain pentene, 2-methylbtuene-2 to represent the branched chain pentene and dilute i-pentane、n-pentane、2-pentene and 2-methylbtuene-2 to 7.6wt% with n-heptane as the feeding oil.

Table 1. :Component and content of C5 raffinate

component	wt%
isobutylene	1.1
1,3-butadiene	4.0
n-butane	0.2
c-butene-2	2.2
3-methylbutene-1	3.7
1,4-pentadiene	4.4
butyne-2	0.1
i-pentane	16.5
pentene-1	17.8
2-methylbutene-1	17.0
isoprene	1.0
n-pentane	19.8
t-pentene-2	7.6
c-pentene-2	3.1
2-methylbutene-2	1.5

Hydrogenation experiment condition of C5 raffinate refers to the first selective hydrogenation reactor of No.4 naphtha cracker and the simulation result of Aspen. We decide initial temperature is 70℃, reaction pressure is 30kg/cm2 and the Liquid Hourly Space Velocity (LHSV) is 18hr-1. The hydrogen purity is the pure hydrogen above 99% and the mole ratio of hydrogen to feed oil is 1.1.The reactor catalyst is mainly choiced according to the first selective hydrogenation reactor of No.4 naphtha cracker and the solvent hydrogenation reactor, it contains A catalyst(Pd 0.3wt%)、 B catalyst (Ni 50wt%) and C catalyst (NiS 10wt%).The catalyst properties are listed in table 2.

Table 2:Catalyst property of C5 hydrogenation.

Catalyst	A	B	C
Active metal	Pd	Ni	NiS
metal,wt%	0.3	50	10
SA, m2/g	115	256	143
PV, mL/g	0.46	0.31	0.56

The experimental products are analyzed by GC/FID and the results are shown in figure 1. The upper chromatogm of GC/FID is feed containing i-pentane、n-pentane、2-pentene(include cis and the trans) 、2-methylbtuene-2 and n-heptane, after the hydrogenation the product only remains i-pentane and n-pentane as down chromatogm of GC/FID . Analysis condition of GC/FID is as follows: oven 35℃ holds 10 minutes, then elevates temperature 10℃/min to 120℃, and holds under this temperature 2 minutes. Both the injector and the detector temperature establish in 280℃, and split ratio is 50:1.

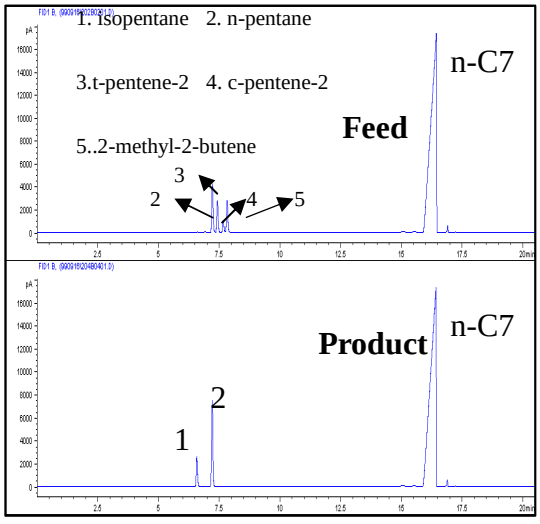

Figure 1:GC/FID chromatogm of C5 feed and hydrogenation product.

In experiment, we increase the product quantity to reduce the C5 volatility which influence the experimental error and calculate conversion rate with heptane as intern standard. The formula is as follows:

$$\textbf{n-Pentene conversion rate} = 1 - \frac{\left.\frac{(tC_5^= + cC_5^=)}{nC_7}\right|_{out}}{\left.\frac{(tC_5^= + cC_5^=)}{nC_7}\right|_{in}}$$

$$\textbf{i-Pentene conversion rate} = 1 - \frac{\left.\frac{2M2B}{nC_7}\right|_{out}}{\left.\frac{2M2B}{nC_7}\right|_{in}}$$

The experiment condition which C5 alkenes content is 7.3wt%, LHSV is the 17.8hr-1, H2/feed mole ratio is 1.1 is proceeded with three kinds of test catalyst, and test results are shown in Figure 2. B catalyst is the best C5 alkenes hydrogenation and pentene conversion rate reach above 99%.Conversion rate of A catalyst to 2-pentene is 92.4%, to 2-methylbutene-2 is 87.6%,but C catalyst only transforms 2-pentene to 35.1%, 2-methylbutene-2 to 20.4%.Conversion rate of n-pentene is better than i-pentene in the three catalysts, and increasing reaction temperature can improve conversion rate.

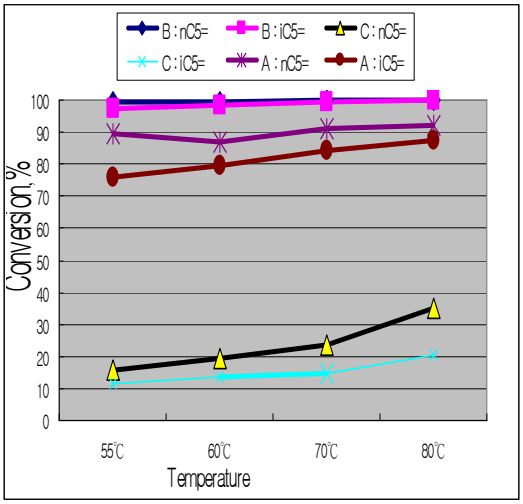

Figure 2:Hydrogenation conversion of n-pentene and iso-pentene at different catalyst.

Pressure at 30kg/cm2 and temperature at 80℃of the hydrogenation reactor can totally saturate pentene ,so we use the solvent plant reactor pressure 12kg/cm2 to make the test under the same temperature. The test results are shown in Figure 3.

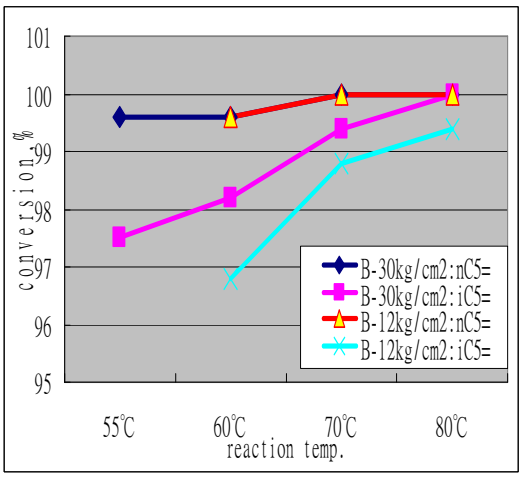

Figure 3:Conversion of C5 hydrogenation at 30kg/cm2 and 12kg/cm2.

In figure 3, activeness influence of n-pentene is small in different pressure, but the i-pentene influence is big. Because the branched chain pentene has steric barrier, it affects the hydrogenation catalyst function. We can elevate the reaction temperature to overcome the steric barrier and increase the i-pentene conversion rate. When reaction temperature is at 80℃, it may completely saturate n-pentene and i-pentene, and conversion rate reach above 99.4%.

3. Conclusion

The pentane may substitute the HCFC for foaming agent, reduce ODP and GWP, and treat as the environmental protection solvent. The C5 raffinate of C5 distillate in pygas oil includes C5 sateurated and C5 olefin which generally mixes into 92 unleaded gasoline. If the C5 raffinate is saturated by hydrogenation process, the product will be used as plastic foaming agent. From our research, C5 raffinate can be completely hydrogenated in the 12kg/cm2 reaction pressure, 80℃ the reaction temperature and LHSV 18hr-1 with B catalyst. The Aspen simulation and economical appraisal result of C5 raffinate hydrogenation process need 1.64 billion NT$ for total investment, and the return rate is 12% after the tax.

4.Acknowledgment

The author expresses his appreciation to the department of technology service in RMRI for sample analysis.

5.Reference

[1] Liang Chenggang, Liu Zhihong.”Appkication of pentane foaming agent as a substitute for CFCs in PU rigid foamed plastics”, Inner Mongolin Petrochemical Industry,volume. 28,pp.26-30,2002.

[2]Wu ZHEN,Guo Qing,”Application research of new green-blowing agents in rigid polyurethane foam”,New Building Materials,pp.42-46,2008-01.

[3]Fang Gongbin, Han Wenyue,Shang Yuxiang,”The development of replacing technology of polyurethane blowing agent used in refrigerator”,Polyurethane Industry,volume 19,No. 4,pp. 37-40,2004.

[4]Shang Yuxiang, Fang Gongbin,”Application of pentane foaming system in polyurethane foam of the refrigerators”, Polyurethane Industry,volume 19,No. 3,pp. 34-37,2004.