

DEHYDROCYCLIZATION OF NORMAL HEPTANE TO TOLUENE USING BI-METALLIC REFORMING CATALYSTS *)

by

A.S. Nasution, M.Sc.

Dehydrocyclization of n-heptane and the influence of benzene on this reaction has been carried out with bi-metallic reforming catalyst at the operating temperature : (from 450^o to 490^oC), pressure (from 10 to 30 kg/cm²), H₂/Hydrocarbon (from 4 to 12 mole/mole) by using a Cata-test unit apparatus.

INTRODUCTION

The rapidly increasing demand for aromatic hydrocarbon as petrochemical feedstock has promoted refiners to seek methods of improving yields of these valuable products.

Catalytic reforming of naphtha is one of the aromatic production from petroleum (1). As paraffins are usually the mayor component in the naphtha feedstocks, thus high conversion of paraffins to aromatic plays an important role.

With the rapid development on the Indonesian industry, the demand of aromatic hydrocarbons for petrochemical feedstock will increase. So in several years to come, an Aromatic Centre will build in Indonesia.

In order to obtain more information about conversion of paraffins to aromatic hydrocarbon, an experiment has been carried out to study the reaction rate of normal heptane dehydrocyclization and the influence of benzene hydrocarbon in this reaction with the operating temperatures : from 450^o to 490^oC, pressures : from 10 to 30 kg/cm² and H₂/HC ratio from 4 to 12 mole/mole by using a bi-metallic reforming catalyst.

A micro-catalytic activity (Cata-test) unit operated in a contineous system was used in these experiments. Gas and liquid product samples taken from gas and liquid samplers respectively were analysed by using a Gas-Liquid Chromatography.

EXPERIMENTAL

Pure grade of normal heptane and benzene were used as feedstocks.

The purified hydrogen, containing impurity less than 0,5% by vol and bi-metallic reformer catalyst were used in this experiment.

Experiment was carried out in a microcata-test unit, without gas recycle, operated at high temperature and pressure with a continuous system (Figure 1)

The volume and inside diameter of the reactor are 200 cc and 19 mm respectively. The reactor temperature is regulated automatically.

Gas and liquid product samples were taken from gas and liquid sampler respectively and these products were then analysed by using Gas-Liquid Chromatography.

*) Presented and proceeding at the Third Pacific Chemical Engineering Congress, Seoul Korea, May 8 - 11, 1983.

RESULTS AND DISCUSSION

Rate of n-heptane dehydrocyclization with various temperatures, pressures and H₂/HC ratio are set up on the Table 1, 2 and 3.

Activation energy of n-heptane dehydrocyclization is calculated by using the following Arrhenius equation,

$$k_1 = A_1 e^{-E/RT}$$

As the rate (r₀) is proportional to the rate constant (k₁), the Arrhenius equation can be written as follows :

$$r_0 \approx k_1 = A e^{-E/RT}$$

Figure 2 shows a plot of log r₀ against 1/T for n-heptane dehydrocyclization. The slope is equal to -E/2,303 R and leads E = 33,688 kcal/mole.

The rate of n-heptane dehydrocyclization is written as follows,

$$r_0 = k_2 P_{C_7H_{16}}^{\alpha} P_{H_2}^{\beta}$$

If H₂/HC ratio is kept constant, the rate becomes,

$$r_0 = k_3 P_T^{(\alpha+\beta)}$$

$$\text{or } \log r_0 = (\alpha + \beta) \log P_T + \log k_3$$

Figure 3 show a plot of log r₀ against log P_T for n-heptane dehydrocyclization. The slope is equal to (α + β) = -0,5041.

If the P_{H₂} is kept constant, the above rate equation becomes

$$r_0 = k_4 P_{C_7H_{16}}^{\alpha}$$

$$\text{or } \log r_0 = \alpha \log P_{C_7H_{16}} + \log k_4$$

Figure 4 shows a plot of log r₀ against log P_{C₇H₁₆} for n-heptane dehydrocyclization. The slope is equal to α = 0,8007.

The reaction order with respect to hydrogen pressure of n-heptane dehydrocyclization is calculated as follows :

$$\beta = (-0,5041) - (0,8007) = -1,3048$$

By substitution the experimental rates (r₀) to the following rate equation;

$$r_0 = A e^{-33.688/RT} P_{C_7H_{16}}^{0.8007} P_{H_2}^{-1.3048}$$

the frequency factor (A) can be calculated, and leads A = 0.86.10⁷.

The rate equation of n-heptane dehydrocyclization becomes;

$$r_0 = 0.86.10^7 e^{-33.688/RT} P_{C_7H_{16}}^{0.8007} P_{H_2}^{-1.3048}$$

Based on the experimental data of the rate equation of n-heptane dehydrocyclization to toluene shows that the rate will be favorable on the following operating conditions :

- . High temperature
- . Low total pressure
- . Low H₂/HC ratio.

As the rate of n-heptane hydrocracking increase at high operating temperature (2) and the rate of coke deposit on the catalyst surface will increase at low total pressure and low hydrogen to hydrocarbons ratio (3), so those three operating conditions have an optimal value.

An other equation of the rate of n-heptane dehydrocyclization can be written as follows :

Without benzene addition,

$$r_1 = k_5 \frac{K_{C_7H_{16}} K_{H_2} P_{C_7H_{16}} P_{H_2}}{(1 + K_{C_7H_{16}} P_{C_7H_{16}} + K_{H_2} P_{H_2})^2}$$

With benzene addition

$$r_2 = k_5 \frac{K_{C_7H_{16}} K_{H_2} P_{C_7H_{16}} P_{H_2}}{(1 + K_{C_7H_{16}} P_{C_7H_{16}} + K_{H_2} P_{H_2} + K_{C_6H_6} P_{C_6H_6})^2}$$

or

$$\left(\frac{r_1}{r_2}\right)^{1/2} = 1 + \frac{K_{C_6H_6} P_{C_6H_6}}{1 + K_{H_2} P_{H_2} + K_{C_7H_{16}} P_{C_7H_{16}}}$$

If n-heptane is sufficiently strongly adsorbed compared to hydrogen, so that (K_{C₇H₁₆} P_{C₇H₁₆}) is much greater than (1 + K_{H₂} P_{H₂}) and the (r₁/r₂)^{1/2}

equation can be written as follows;

$$\left(\frac{r_1}{r_2}\right)^{1/2} = \frac{K_{C_6H_6}}{K_{C_7H_{16}}} \frac{P_{C_6H_6}}{P_{C_7H_{16}}} + 1$$

Figure 5 show a plot of $(r_1/r_2)^{1/2}$ against $(P_{C_6H_6}/P_{C_7H_{16}})$ with operating temperature : 450^o; 470^o and 490^oC, for n-heptane dehydrocyclization.

The slope is equal to $(K_{C_6H_6}/K_{C_7H_{16}})$ and leads $(K_{C_6H_6}/K_{C_7H_{16}})$ for operating temperature 450^o; 470^o and 490^oC are 1.6490; 1.3503 and 1.1764 respectively.

Figure 4 shows a plot of $\log(K_{C_6H_6}/K_{C_7H_{16}})$ against $(1/T)$. The slope is equal to $-(\Delta H/2.303 R)$ and lead $\Delta H = 9,268$ kcal/mole. And the calculated frequency factor (A_2) is obtained $A_2 = 0.26.10^{-3}$.

Based on the experimental data show that the constant adsorption rate of benzene is higher compared to n-heptane, and the difference head of adsorption of those two hydrocarbons is $\Delta H = 9.268$ kcal/mole.

As the adsorption of n-heptane feedstock and benzene is competitive (1) and the constant adsorption rate of benzene is higher than the constant adsorption rate of n-heptane, the rate of n-heptane dehydrocyclization will decrease by presence of benzene or other aromatic hydrocarbons (4).

By development the structure of active metal site of bi-metallic reforming catalyst, the negative effect of benzene and other aromatic hydrocarbons on the rate of n-heptane dehydrocyclization can be reduced.

CONCLUSION

Base on the experimental data show :

The rate of n-heptane dehydrocyclization is,

$$r_0 = 0.86.10^7 e^{-33.688/RT} \frac{0.8007}{P_{C_7}} \frac{-1.3048}{P_{H_2}}$$

The ratio of the adsorption constant rate between benzene and n-heptane at operating temperature : 450^o, 470^o are 1.6490; 1.3503 and 1.1764 respectively, which can be written as following equation

$$\frac{K_{C_6H_6}}{K_{C_7H_{16}}} = 0.26.10^{-3} e^{9.268/RT}$$

It suggest that the rate of n-heptane dehydro cyclization to toluene has an optimal operating condition : i.e. temperature, pressure and hydrogen to hydrocarbon ratio for a given catalyst.

Benzene and other aromatic hydrocarbons can reduce the rate of n-heptane dehydrocyclization.

NOTATION

A_1 and A_2 = are the frequency factors;
 C_6H_6 and C_7H_{16} = are benzene and normal heptane respectively.

E = is activation energy-kcal/mole
 H_2 , HC and H_2/HC = are hydrogen, hydrocarbons and the mole ratio between H_2 and hydrocarbons respectively.

k_1 , k_2 , k_3 , k_4 and k_5 = are the rate constants.
 K_{H_2} , $K_{C_6H_6}$ and $K_{C_7H_{16}}$ = are the constant absorption rate of hydrogen, benzene and normal heptane respectively.

P_T , P_{H_2} , $P_{C_6H_6}$ and $P_{C_7H_{16}}$ = are the total pressure and pressure of hydrogen, benzene and normal heptane respectively -kg/cm².

r_0 , r_1 and r_2 = are the reaction rates or the rate.

R = is a gaseous constant
 T = is absolute temperature -^oK
 $(\alpha + \beta)$, α and β = are total order and order with respect to hydrocarbon and hydrogen of reaction respectively.

$\Delta H_{C_6H_6}$, $\Delta H_{C_7H_{16}}$ and ΔH = are the absorption heat of benzene, normal heptane and their difference.

Influence of temperature on the rate of n-heptane dehydrocyclization ($r \cdot 10^4$ gr-mole/hour gr-catalyst) at $P = 20 \text{ kg/cm}^2$ and $H_2/HC = 4$ mole/mole.

Table 1

$T^\circ\text{C}$	450 ^o	470 ^o	470 ^o	490 ^o C
r_o	57.46	108.62	110.06	196.39

Influence of pressure on the rate of n-heptane dehydrocyclization ($r \cdot 10^4$ gr-mole/hour gr-catalyst) at $T = 450^\circ\text{C}$ and $H_2/HC = 4$ mole/mole.

Table 2

$p \text{ kg/cm}^2$	10	20	20	30
r_o	125.84	108.6	110.06	69.58

Influence of H_2/HC on the rate of n-heptane dehydrocyclization ($r_o \cdot 10^4$ gr-mole/hour gr-catalyst) at $T = 450^\circ\text{C}$ and $P = 20 \text{ kg/cm}^2$.

Table 3

H_2/HC mole/mole	4	4	8	12
r_o	108.62	110.06	97.2	48.5

Influence of benzene pressure with operating various temperatures on the rate of n-heptane dehydrocyclization ($r_o \cdot 10^6$ gr-mole/hour gr-catalyst) at $P = 20 \text{ kg/cm}^2$ and $H_2/HC = 4$ mole/mole.

Table 4

$T^\circ\text{C}$	Benzene partial pressure, $P_{C_6H_6} = \text{kg/cm}^2$			
	1.58	2.33	3.06	3.50
450 ^o	990.0	376.6	116.8	36.0
470 ^o	2287.5	802.9	241.1	93.2
490 ^o	3557.31	2493.7	742.9	203.7

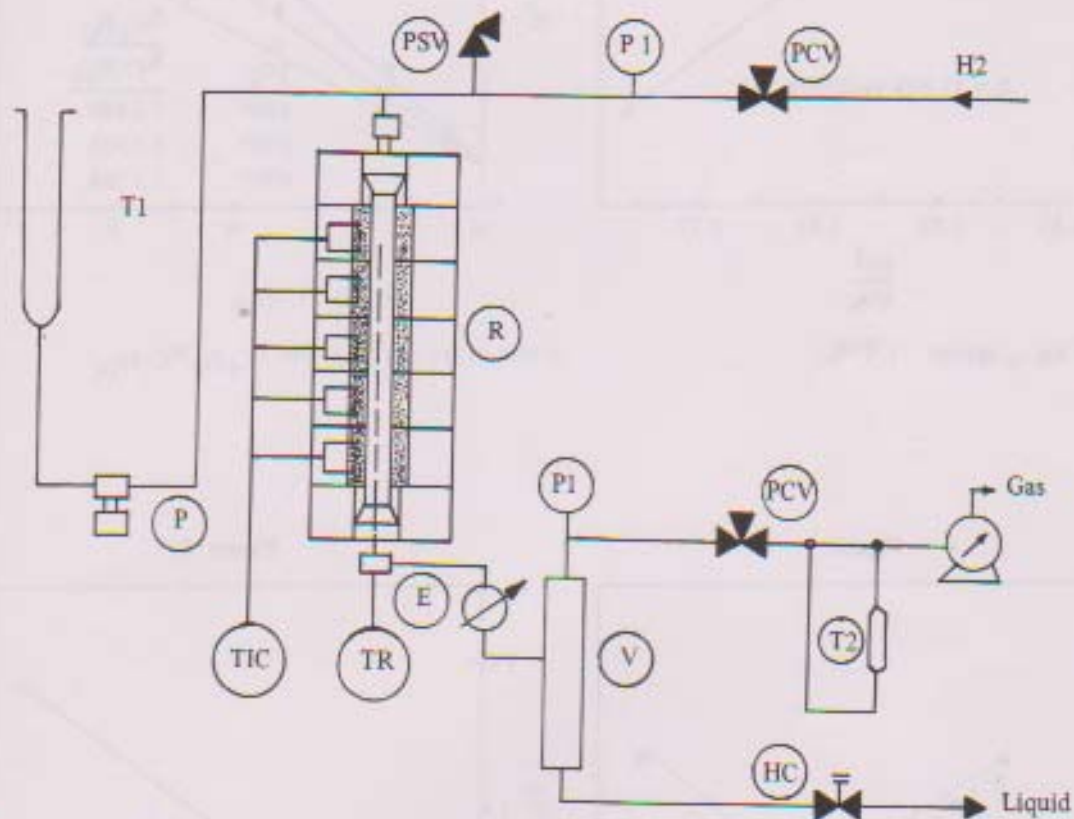
LITERATURE CITED

1. Wuthier, P., *Raffinage et Genie Chimique*, Edition Technip, Paris 15e, France (1965).
2. Hettinger, W.P. and Keith, C.D., *Ind. Eng. Chem.* 47, (4), 719 (1955).
3. Heinz Heinemann and Mills, G.A., *Ind. Eng. Chem.*, 45, (1), 140 (1953).
4. Germain, J.E., *Catalytic Conversion of Hydrocarbon*, Academic Press, London (1969).

Figure 1

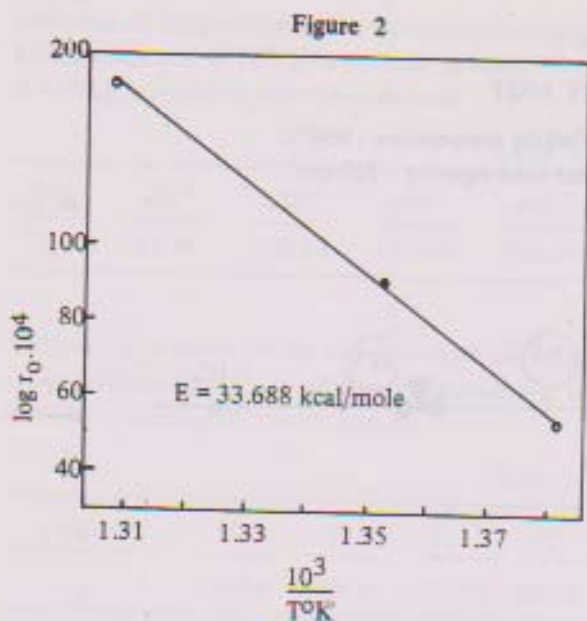
CATATEST UNIT

Working pressure : 150 bars-Working temperature : 550°C
 Liquid flow : 750 cc/h-Contact tube capacity : 220 cm³

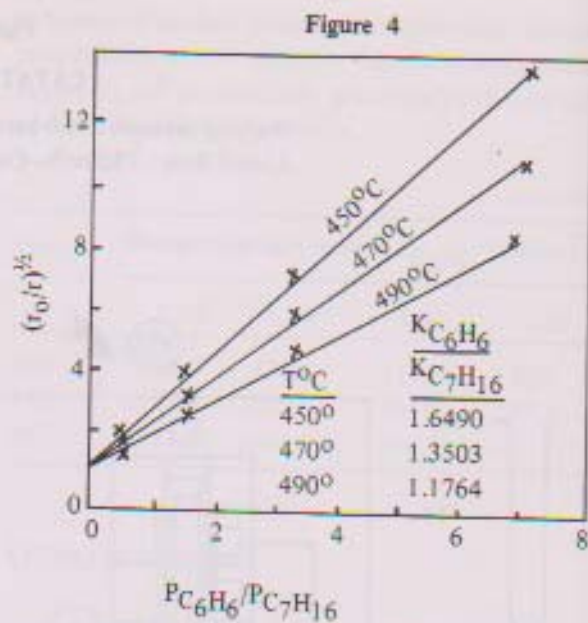


- E — Condenser
- FT — Gas meter
- HC — Manual valve
- P — Adjustable flow pump
- PCV — Pressure regulator
- P1 — Pressure gauge
- PSV — Pressure safety valve

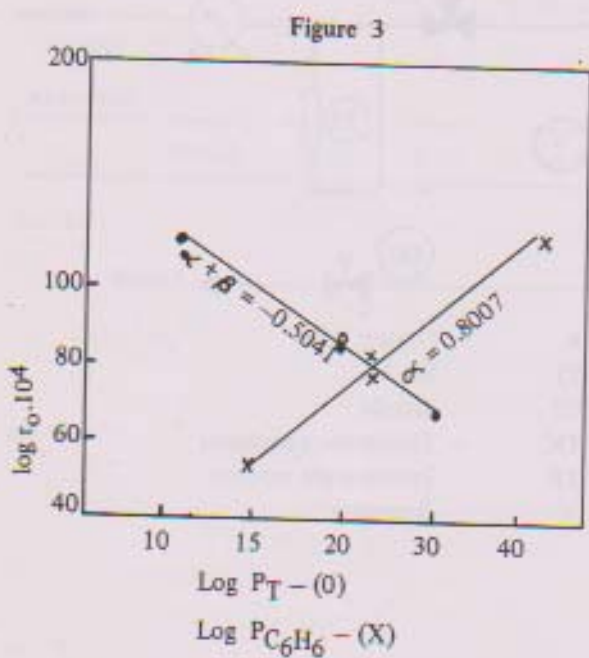
- R — Contact tube
- T1 — Batch
- T2 — Sample
- TIC — Temperature regulator
- TR — Temperature recorder
- V — Separator



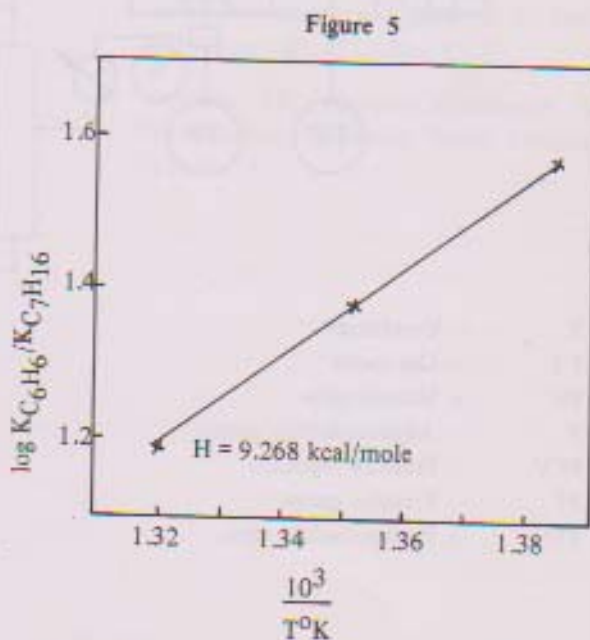
A plot of $\log r_0$ against $1/T^0K$.



A plot of $(r_1/r_2)^{1/2}$ against $P_{C_6H_6}/P_{C_7H_{16}}$.



A plot of $\log r_0$ against $\log P_T$ and $\log P_{C_6H_6}$.



A plot of $\log K_{C_6H_6}/K_{C_7H_{16}}$ against $1/T^0K$.

RESEARCH AND DEVELOPMENT CENTRE FOR OIL AND GAS TECHNOLOGY

IS ALWAYS AT YOUR SERVICE FOR :

- * GRAVIMETRIC SURVEY
- * MICRO PALEONTOLOGIC ANALYSIS
- * ROCK DESCRIPTION
- * CORE ANALYSIS
- * PVT ANALYSIS
- * CRUDE OIL EVALUATION
- * PRODUCT QUALITY CONTROL
- * CHEMICAL ANALYSIS
- * CORRELATION STUDIES
- * OTHER LABORATORY ANALYSIS

PLEASE CONTACT :
PPPTMGB "LEMIGAS"
Cipulir, Kebayoran Lama
P.O. Box 89/JKT.
Jakarta 10002
Phone : 734422
Telex : 47150 - 47172