

Optimization of n-Hexane Reforming Using Taguchi Orthogonal Array Design

(Pengoptimuman Pembentukan Semula n-Heksana Menggunakan Reka Bentuk Taguchi Tatasusunan Ortogon)

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ABSTRACT

Taguchi orthogonal array design, a statistical software is applied to n-hexane reforming. The purpose is to identify the most significant process variable in reforming conditions favouring n-hexane conversion to high aromatics and isomers and low cracked and coke precursor reformat products. Actual experimental data were used for this study. Three process variables i.e. temperature, contact time and hydrogen partial pressure were investigated. From the study it was found that the contact time was the most critical operating parameter for n-hexane conversion followed by reaction temperature and hydrogen partial pressure. It was also noted that enhanced n-hexane reforming conversion can be achieved by operating the process at reaction temperature 723 K and contact time 7.1 min with a H₂ partial pressure 300 kPa. For selectivity to aromatics and isomers lower contact time of 1.07 min with intermediate hydrogen partial pressure of 300 to 500 kPa operating at a reaction temperature of 723 K is most favourable.

Keywords: Aromatic; coke; conversion; n-hexane reforming; selectivity

ABSTRAK

Reka bentuk Taguchi tatasusunan ortogon, satu perisian, statistik telah digunakan untuk pembentukan semula n-heksana. Tujuan utama adalah untuk mengenal pasti pemboleh ubah yang mementingkan proses pembentukan semula n-heksana bagi menghasilkan aromatik dan isomer yang tinggi pengeluarannya dan kurangkan produk retak dan kok. Data uji kaji telah digunakan untuk kajian ini. Tiga pemboleh ubah telah dikaji iaitu suhu, sentuhan masa dan separa tekanan hidrogen. Dicapai bahawa sentuhan masa adalah parameter yang paling penting dalam operasi penukaran n-heksana diikuti oleh suhu tindak balas dan separa tekanan hidrogen. Selain itu, penukaran pembentukan semula n-heksana boleh dipertingkatkan dengan menjalankan proses pada suhu 723 K, dengan sentuhan masa selama 7.1 min dan pada 300 kPa separa tekanan hidrogen. Untuk mementingkan penghasilan produk aromatik dan isomer, keadaan terbaik adalah apabila sentuhan masa ialah 1.07 min, separa tekanan hidrogen yang sederhana iaitu di antara 300 kPa sehingga 500 kPa dan pada suhu 723 K.

Kata kunci: Aromatik; kok; operasi penukaran; pembentukan semula n-heksana; penghasilan produk

INTRODUCTION

Classical factorial method of analysis in catalytic processes involving many process variables requires numerous experiments data for optimization purposes. Classical statistical methods increases consumption of valuable and expensive catalyst (fresh and spent) tagged up with expensive catalyst data analysis. Apart from the cost, the time is also extended due to increase number of analysis. In classical statistic method, if the number of experiments to be carried out is 'N' and the number of levels or factors (process variables) is 'm', this can be translated by the equation $N=L^m$. Some of the experiments carried out may prove less significant or redundant. Omitting these less significant experiment or process variables gives huge saving and reduces the time frame for good analytical results and prediction. Selection of the favourable

experiments can be obtained by determining the order of importance (% quantity contributions) of each process variable used. A good statistical design of experiment tool which is capable perform these quantification is highly favourable. Using classical statistical methods for this purpose is not an easy task as indicated by Mahamuni and Adewuyi (2010).

For the present study three parameters i.e. H₂ partial pressure, reaction temperature and contact time were analysed for optimization of n-hexane reforming. The challenge posed here was to identify which of these process variables is significant to maximise favoured aromatics and isomers over unfavoured cracked and coke precursor for n-hexane reforming process. For this purpose a Design-Expert software (version 6.0.6) using Taguchi orthogonal array design was selected

EXPERIMENTAL TECHNIQUE

N-HEXANE REFORMING EXPERIMENT SET-UP

The *n*-hexane reforming experiment was carried out in a high pressure fixed bed micro-tubular reactor attached to an on-line GC with a TCD and FID detection system. *N*-hexane was pumped into the micro-reactor using a high pressure pump to react with an industrial activated Pt Al₂O₃ based catalyst at pre-set conditions. The experimental detail has been reported elsewhere (Ismail 2011).

PROCESS VARIABLES AND PRODUCT CLASSIFICATION FOR N-HEXANE REFORMING

The process variables chosen for this study were limited to process temperature of 623 to 723 K, H₂ partial pressures of 300 to 700 kPa and contact time of 1.02 to 7.1 min. Process temperature influences the rate of reaction, while H₂ partial pressure and contact time influence the rate of cracking. For this purpose, three measurements for each process variable were taken; process temperatures of 623, 673 and 723K, H₂ partial pressures 300, 500 and 700 kPa and contact time of 1.02, 1.78 and 7.11 min were chosen.

Reformats arising from the *n*-hexane reforming reactions were basically divided into either reversible or irreversible reaction products. These products were then divided into 4 main groups namely cracked products (reversible), all irreversible reformates. The cracked species are all those reforming products which are saturated ranging from C1 to C4 *n*-alkanes, while the coke precursors species include C2 to C6 olefins, others like the isomers refer to iso-C5 and iso-C6; the aromatics are basically benzene. Although toluene and xylene may

be present, it is not detected by the GC. Table 1 lists the various products described above. It should be noted that *n*-C6 is the feedstock for the above reforming reaction.

REFORMING CONDITIONS FACTORIALS

For this purpose Taguchi Orthogonal Array Design Expert Software version 6.0.6 was selected. To start off, 3 factors and 3 levels were chosen. The factors chosen were temperature (A:A), H₂ partial pressure (B:B) and contact time (C:C). The level was set such that '1' represent the highest *n*-hexane conversion for each factor (temperature, pressure and contact time) and '3' the lowest. This is tabulated in Table 2. The experimental data were taken from Ismail (2011).

CONVERSION OF N-HEXANE REFORMING USING THE TOAD METHOD

Having set the factors and level for the Taguchi orthogonal array design or TOAD simulation, three factors were chosen (reaction temperature, H₂ partial pressure and contact time). For each factor three levels using a standard L9 orthogonal array based on Kul and Cetinkaya (2010) model was used. Each row of the matrix was matched to the average conversion at the specified conditions as highlighted in Table 3.

Next the statistical analysis of these results was carried out using analysis of variance (ANOVA) and tabulated in Table 4. The purpose of ANOVA is to investigate the factors which significantly affect the response factor which in turn grades the percentage contribution for each process variables used in this study i.e. temperature, H₂ partial pressure and contact time.

TABLE 1. Grouping of products from reforming reactions

Reforming Product Group			
Cracked	Coke precursors	Isomers	Aromatics
Methane	Ethylene	Iso-butane	Benzene
Ethane	Propylene	Iso-pentane	-
<i>n</i> -Propane	Iso-propylene	Iso-hexane	-
<i>n</i> -Butane	others	Cyclo hexane	-

TABLE 2. Reforming conditions factors and levels

Factor	Levels		
	1	2	3
A:A Temperature (K)	723	673	623
B:B Pressure (KPa)	700	500	300
C:C Contact time (Min)	7.11	1.78	1.02

TABLE 3. L9 TOAD Method based on Kul & Cetinkaya (2010)

Run	Experimental Conditions			<i>n</i> -hexane Conv. (%)
1	2	3	1	67.1
2	1	1	1	66.9
3	2	2	3	43.5
4	3	2	1	60.0
5	3	3	2	54.6
6	3	1	3	32.9
7	1	2	2	65.8
8	1	3	3	55.5
9	2	1	2	54.2

TABLE 4. The ANOVA Analysis of *n*-Hexane Conversion

Factors	DOF	Sum Sqrs	F value	Prob>F	Contributions (%)
Temperature	2	278.2	66.55	0.0148	26.58
H ₂ pressure	2	92.28	22.07	0.0433	8.816
Contact time	2	672.0	160.7	0.0062	64.20
Error	2	4.180	2.100		0.399
Total	8	1047	-		100

Based on the 'model F' value from Table 4, it can be seen that the average for all 3 factors is 83.13. This implies that this model is highly significant and there is only a 2.1% probability that this large 'F-value' could result from noise effect. Further, all 3 factors or process variable are also significant model terms since 'Prob>F' is less than 0.05%.

RESULTS AND DISCUSSION

Contact time is the most significant process variable affecting the *n*-hexane conversion with a contribution of 64.2%, followed by reaction temperature (26.58%) and H₂ partial pressure of 8.82% for H₂ partial pressure (Table 4 & Figure 1). Further, to determine the optimum contribution from each of the process variables, individual analysis was done to observe the sensitivity to changing process variable conditions (Figure 2).

N-hexane conversion increases with contact time. From 1.78 to 7.11 min the conversion increases at a much slower rate. The same trend is observed for the reaction temperature and contact time where highest rate is observed at 723 K and lowest at 623 K.

As for hydrogen partial pressure (B: B), the conversion follows a reverse pattern to that of contact time and reaction temperature. Highest conversion of *n*-hexane is at 300 kPa and lowest at 700 kPa. This may indicate that for optimum operating conditions for *n*-hexane reforming conversion is to operate the process with a contact time of 7.1 min, temperature of 723 K with a H₂ partial pressure of 300 kPa.

OPTIMIZATION OF AROMATICS REFORMATE % YIELD USING TOAD METHOD

The next step is to maximize the desirable products (aromatics and isomers) and minimize the undesirable (cracked and coke precursors) reformat product. It should be noted that desirable products improve octane number, while the undesirable products decreases it.

The TOAD method is again used to find the optimum level for aromatic yield. The results obtained are presented in Figure 3. From the same figure be can be seen that; hydrogen partial pressure (51.9%) is the major contributor, followed by contact time (32.7%) while reaction temperature (<1%) has an insignificant role it will be omitted in the discussion and in Figure 4.

Figure 4 shows the effect of contact time and H₂ partial pressure for enhanced aromatics production. From the same figure, it is seen that, the highest yield for aromatics for H₂ partial pressure is 300 kPa. This is in agreement with Antos et al. (1995) who reported that; lower H₂ partial pressure favours dehydrogenation of naphthenes and dehydrocyclization of paraffin and at the same time lowers the activity of the catalyst. Therefore the choice of hydrogen partial pressure is an important matter for balancing product yields against deactivation rates as recommended by Liu (1995). Higher contact time (7.1 min) favours highest selectivity for aromatic production. Although the reaction temperature is shown to have an insignificant effect in the present work, Long et al. (2008), indicated that higher reaction temperatures induces increased production of aromatics which translates to increases octane rating. However, Agbajelola and

Aberuagba (2007), warn that this will reduces catalyst life. In view of that, an optimum temperature condition should be identified for the final TOAD analysis.

OPTIMIZATION OF ISOMER REFORMATE YIELD USING TOAD METHOD

The TOAD method for optimization of isomer reformat yield is calculated and presented in Figure 5. From the figure it can be observed that the contributions from all three process variable factors are significant, unlike the earlier study on aromatics yield. Contact time has the highest impact (35.75%), followed by reaction temperature (25.31%) and finally H_2 partial pressure (18.67%).

Plots of the influence of variation of these process variables are shown in Figure 6. From the plots, it can be seen that isomer yield increased with increasing temperature reaching the maximum yield at 723 K. Contact time follows a different trend where the isomer reformat production is low at both high and low contact time, but maximizes at 1.78 min. This is in agreement with findings of Talukdar et al. (2001) who reported that increasing the contact or residence time of the reactant on the catalyst surface leads to an enhanced yield of the skeletal isomers. Longer residence times result in both cracking and polymerization of these products.

Although the effect of H_2 partial pressure on isomer yield is less significant as compared with reaction temperature and contact time, isomers yield is favoured by lower H_2 partial pressure.

Based on the above findings, the optimum process conditions for isomers production is operating at a reaction temperature of 723 K, 1.78 min contact time and using H_2 partial pressure of 300-500 kPa.

MINIMIZING OF CRACKED REFORMATE YIELD USING TOAD METHOD

In the earlier case maximizing of aromatic and isomer reformat was the main priority. Minimizing cracked reformat is the main priority in the following investigation. In view of this TOAD analysis was again applied to the 'cracked' product reformat to determine the main process variable contributors. The result is presented in Figure 7. From this figure it can be seen that the contact time is the major contributor where controls -73.9%, followed by reaction temperature (15.0%) and H_2 partial pressure (8.4%).

Cracked reformates yield decreases octane number and therefore should be eliminated or minimised. In order to have a better understanding on the effect of contact time and temperature, a plot of its variation is presented in Figure 7.

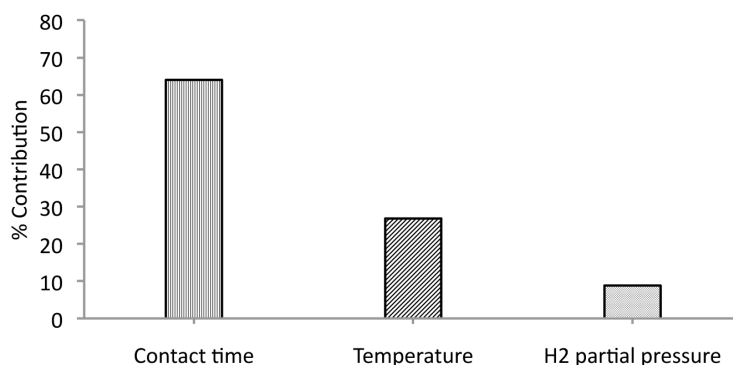


FIGURE 1. Significance of individual factors on variation in *n*-hexane conversion

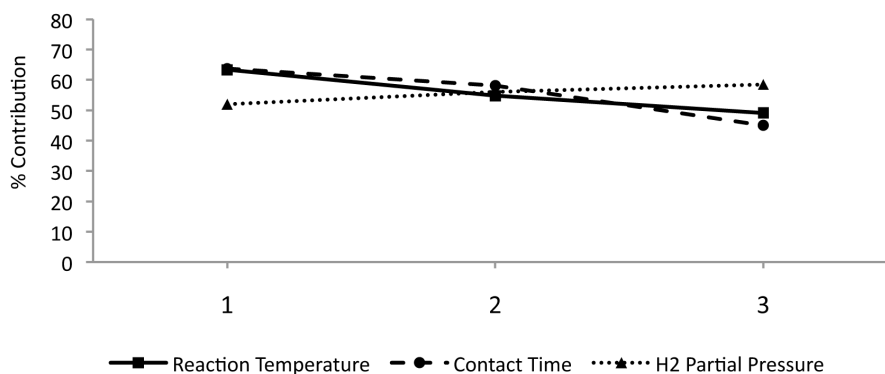


FIGURE 2. Effect of reaction temperature (1=723 K, 2=673 K & 3= 523 K), contact time (1= 7.1 mins, 2=1.8 mins, 3= 1.02 mins) and hydrogen pressure (1= 700 kPa, 2=500 kPa & 3= 00 kPa) on *n*-hexane conversion

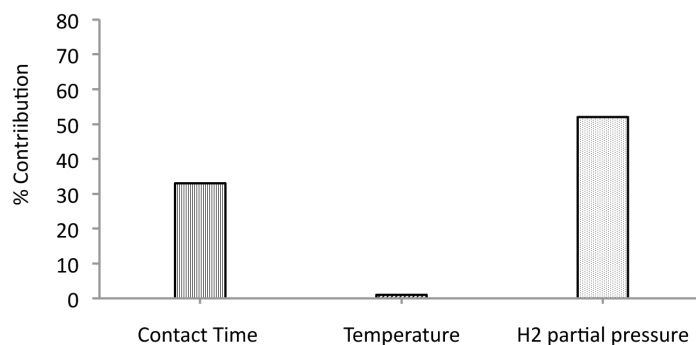


FIGURE 3. Percentage contribution of individual factors for aromatics yield

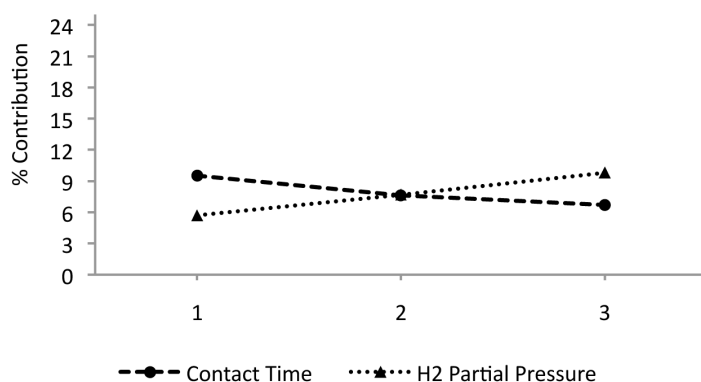


FIGURE 4. Effect of contact time (1= 7.1 mins, 2=1.8 mins, 3= 1.02 mins) and hydrogen pressure (1= 700 kPa, 2=500 kPa & 3= 00 kPa) on aromatic yield

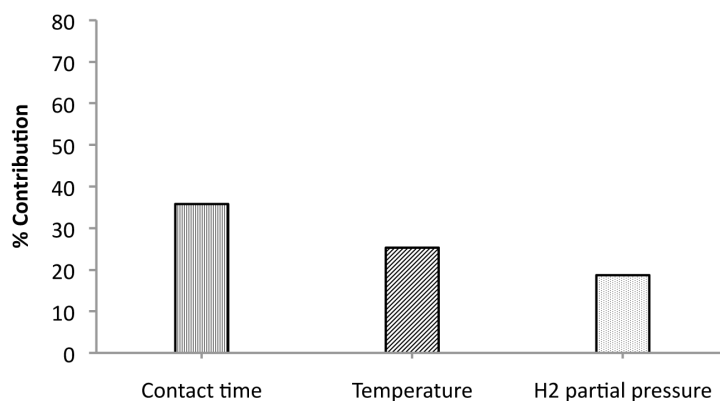


FIGURE 5. Percentage contribution of individual factors on isomers yield

From Figure 7, it can be seen that cracked product reformates decrease with contact time posting the lowest value at 1.02 min and highest value at 7.1 min. The same is observed for reaction temperature i.e. its lowest is at 623 K and highest at 723 K. This finding is in agreement with that of Aberuagba (2000) where he reported that lower contact time and reaction temperature yields lower cracked products. Aberuagba (2000) also reported that H_2 partial pressure does not greatly affect the cracked reformat product yield, but higher H_2 partial pressure favours these undesired products.

Based on this information, it can be assumed that the process should be operated on a lower contact time (1.02 mins) and reaction temperature (623 K) and probably lower H_2 partial pressure (300 KPa) to minimize cracked reformat product yield.

MINIMIZING COKE PRECURSOR REFORMAT YIELD USING TOAD METHOD

The same procedure as the other reformates products mentioned above was carried out for the coke precursors.

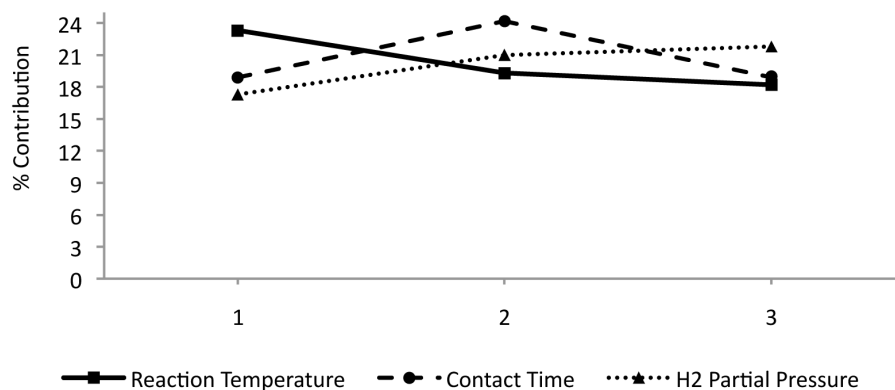


FIGURE 6. Effect of reaction temperature (1=723 K, 2=673 K & 3= 523 K), contact time (1= 7.1 mins, 2=1.8 mins, 3= 1.02 mins) and hydrogen pressure (1= 700 kPa, 2=500 kPa & 3= 00 kPa) on isomer yield

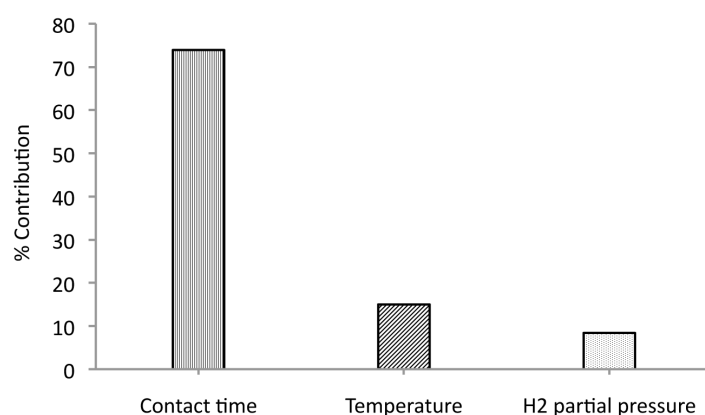


FIGURE 7. The percentage contribution of individual factors on 'cracked' yield

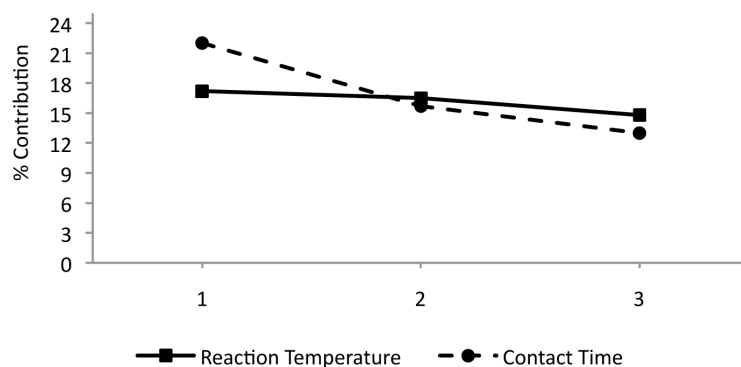


FIGURE 8. Effect of reaction temperature (1=723 K, 2=673 K & 3= 523 K) and contact time (1= 7.1 mins, 2=1.8 mins, 3= 1.02 mins) on 'cracked' yield

The results are presented in Figures 9 and 10. From Figure 9 it can be seen that the major contributor which favours coke precursors is contact time (68.75%), followed by reaction temperature (20.7%) and to a lesser extent, H₂ partial pressure (7%).

Here too, H₂ partial pressure has a minor effect on the overall process, it will be of low priority and the discussion will be tailored to the contact time and reaction temperature (Figure 10).

Decreasing contact time decreases the coke precursor yield (Figure 10). The same is also true for temperature. As mentioned by Brillis and Manos (2003), increase in reaction temperature increases the desorption rate of coke precursor. Antos et al. (1995) also reported yield of unsaturated products (coke precursors) also increases with increasing temperature. Although the effect of H₂ pressure is not a significant factor in this study, others like Liu (1995), reported that hydrogen inhibits the

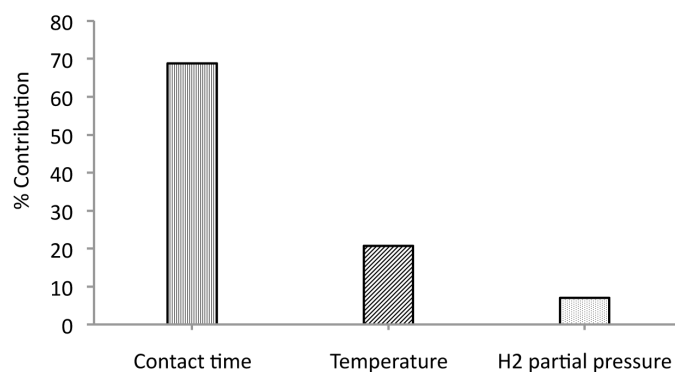


FIGURE 9. The percentage contribution of individual factors on variation in coke precursor's yield

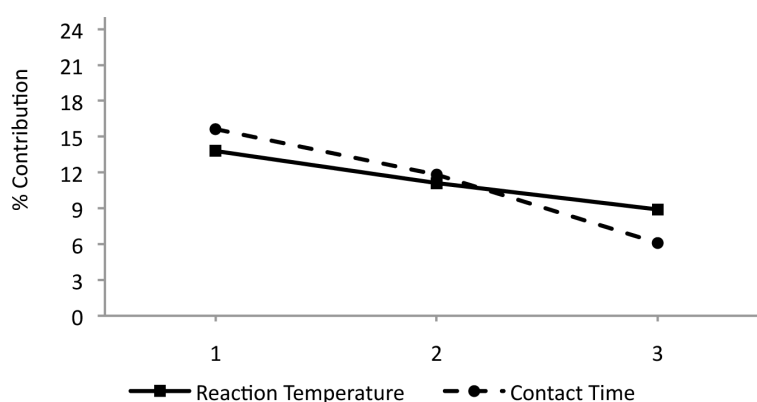


FIGURE 10. Effect of reaction temperature (1=723 K, 2=673 K & 3= 523 K) and contact time (1= 7.1 mins, 2=1.8 mins, 3= 1.02 mins) on 'coke precursor's yield

dehydrogenation reaction. This accounts for a decrease in the deactivation of the catalyst by coking. Based on the above findings, elimination or reduction of coke precursors reformat is best obtained when the process is operated at lower contact time (1.02 min), reaction temperature (623 K) and intermediate H₂ partial pressure (300-500 kPa).

CONCLUSION

The TOAD statistical was successfully used as a tool to identify the trend towards the most significant process variable in reforming conditions favouring *n*-hexane conversion with high aromatics and isomers production. From the above results and findings it can be concluded that for *n*-hexane reforming favouring aromatics and isomers while reducing cracked and coke precursor reformates, the most important process variable is contact time followed by reaction temperature and to a lesser extend H₂ partial pressure. The optimum reforming condition tailored to the desired aromatics and isomers products is to operate at 1.7 min contact time with a reaction temperature of 723 K and 300 kPa H₂ partial pressure.

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REFERENCES

- Aberuagba, F. 2000. Aromatization of Heptene-2 on Pt/Al₂O₃ Catalysts. *Reaction Kinetic Catalysis Letters* 70: 243-249.
- Agbajelola, D.O & Aberuagba, F. 2007. *n*-Hexane Aromatization Over Pt/Al₂O₃ under helium and hydrogen diluents. *AU Journal of Technology* 10(4): 264-270.
- Antos, G. J., Aitani, J., & Parera, M. 1995. *Catalytic Naphtha Reforming Science and Technology*. 1st. Ed, New York: Marcel Dekker.
- Brilliss A.A & Manos G. 2003. Coke Formation During Catalytic Cracking of C8 aliphatic hydrocarbons over ultrastable Y zeolite. *Industrial & Engineering Chemistry Research* 42: 2292-2298
- Ismail, R.A.M. 2011. Optimization of *n*-hexane reforming and kinetics of catalyst regeneration. MSc thesis Universiti Teknologi PETRONAS, Malaysia (unpublished).
- Kul, M. & Cetinkaya, U. 2010. Application of the Taguchi Orthogonal Array Design to Cr (VI) Solvent extraction. *Minerals and Metallurgical Processing* 2: 102-109.

- Liu, K. 1995. Reaction and coking kinetics of n-heptane catalytic reforming; the development of a new vibrational microbalance and application for *in-situ* determination of catalytic reforming reaction and coking kinetics. PhD thesis, New York City University (unpublished).
- Long H., Wang, X.S., Sun, W.F. & Guo, X.W. 2008. Conversion of n-octene over nanoscale HZSM-5 zeolite *Catalyst Letters* 126: 378–382.
- Mahamuni, N.N. & Adewuyi, Y.G. 2010. application of taguchi method to investigate the effects of process parameters on the transesterification of soybean oil using high frequency ultrasound. *Energy Fuels* 24: 2120–2126.
- Talukdar A.K., Bhattacharyya, K.G., Baba, T. & Ono, Y. 2001. 1-hexene isomerization and n-hexane cracking over HMCM-22, *Applied Catalysis A: General* 213: 239–245.

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