Catalytic Cracking of Pentenes in MFI Zeolite: Activation Energy and Reactor Volume Decrease

Klaus A. Serny T.[1*], Pablo J. Baricelli[1], Milexi J. Pacheco M.[1], Luis G. Melean[1], Merlín Rosales[2].
[1] Universidad de Carabobo, Facultad de Ingeniería, Centro de Investigaciones Químicas. Valencia, Venezuela
[2] Universidad del Zulia, Facultad Experimental de Ciencias, Laboratorio de Química Inorgánica. Zulia,
Venezuela
kserny@gmail.com

Abstract: The cracking of pentenes has been investigated at 773 and 873 K in modified MFI zeolite to produce ethylene and propylene. The activation energy showed a significant reduction for this investigation. Additionally, it has been evidenced the important role of the diffusion phenomenon and catalyst technical aspect on the processing of pentenes to produce ethylene and propylene proposing a mathematical model for the design of catalytic reactor achieving a 15% reduction in the volume of the reactor compare to obtained volume with the conventional design. This investigation opens the opportunity to explore new designs of catalysts taking in count intrinsic reactivity, diffusion transport and physics parameters of catalyst which play an important role in the reaction kinetic and reactor design in order to obtain a reduction in the reactor volume more than 15%, 20% on saving construction cost and supplied energy to process.

Key words: cracking, ethylene, pentene, propylene, activation energy, design reactor.

1. Introduction

Light olefins are commonly manufactured by steam pyrolysis of hydrocarbons such as ethane, propane or naphtha. The production of light olefins from light naphtha using a pyrolysis process has been studied and developed in the literature and industry [1], supporting its kinetic and thermodynamic parameters which are all well understood [2-3]. Belohlav et al. [4] compared four types of reactors, taking in count their individual conversions in the radiation, adiabatic and cooling areas, finding a better conversion for the design "long single-row coil" *versus* the "split coils and riser"; with the latter, they were achieved lower yields operating at short residence time (0.1 s) and high temperatures (> 1073 K) which involves a high consumption of energy.

In order to optimize the process to manufacture products such as ethylene and propylene, it is important to study the process carrying out it at lower temperatures in a heterogeneous medium using a porous solid with the intention of obtain a greater selectivity and conversion into the desired products and a lower supplied energy in the process.

In 1999, Redondo et al. [5] report a theoretical study of pentene cracking on zeolites showed the possibility of using the flow of C5 from a refinery to manufacture products of petrochemicals interest, such as propylene and ethylene. These products could feed the petrochemical industry to produce thermoplastic polymers such as polypropylene and polyethylene, long-chain polymers which are softer when heated and, therefore, can be molded under pressure; they represent the 80% of the total consumption of polymers worldwide.

In its report, Chen and co-workers [6], develop a technology for processing a C5 stream and produce ethylene and propylene, separately, assuming a C2/C3 ratio of 2 and a conversion that could go up to 80% for cracking of the C5 olefins using a commercial additive in the reactor of a FCC unit with the rest of the multi-component mixture in its feed. However, as reported Bortnovsky et al. [7] and Sedran and de la Puente [8], the conversion achieved was just 15%, obtaining only propylene; it had the disadvantage of generating cracked gas that could impact the operation of the compression system in the unit and decrease the propylene mixed into the C3 stream available to the alkylation unit

The knowledge of the diffusion coefficients of the molecules of reactants and products within the structure of a heterogeneous catalyst is of up most importance to understand their kinetic behaviour, to propose new designs of catalysts, to optimise the operating conditions and to improve the design of catalytic reactors [9].

Redondo et al. [5], trough theoretical studies raised the possibility of generating two smaller species of hydrocarbons (ethylene and propylene) through an intermediate "carbenium ion" formed when the hydrocarbon is adsorbed on zeolites. In correspondence Rodriguez et al. [10] conducted experimental trials to evaluate the adsorption of propylenes on zeolites, showing the importance of considering the phenomenon of diffusion in order to correct the mathematical models used. Others recent investigations, Artur Ratkiewicz, [11], Chen et al. [12], Mazar, [13], Frash et al. [14], Qingbin Liand and Allan East [15], Ken C. Hunter and Allan L.L. East [16] related to study the beta scission reactions in alkyl radicals concurred on the considerations mechanistic such as the transition states are via carbenium ion, the start and end state are represented for alkoxy species with covalent bond between carbon atom from hydrocarbon and zeolite oxygen. It is noted the studies that they have done widely about the activation energy calculations using density functional theory protocols and others related methods.

According to Kärger and Vasenkov [17], the chemical conversion has an intimate relationship with the diffusion process in heterogeneous catalysis, which occurs because the performance of the catalyst depends on the rate of conversion within the catalyst (intrinsic reactivity) and the molecular exchange rates between the particle and its environment. The smallest of these velocities dominates the overall process; this means that the total conversion cannot proceed faster than the velocity allowed by the transport of the molecules involved.

Traditionally, the design of catalytic reactors, from the process point of view, has been carried out using the estimated volume of catalyst with previous knowledge of feed rate, feed composition, conversion and reaction rate from experimental data. In others words, the catalyst technical information has been ignored predominating the operational technical information of the process.

On the basis of these antecedents, in the present work we studied the cracking of pentenes at different temperatures supported on a porous solid to produce ethylene and propylene and propose a mathematical model for the optimize design of a catalytic reactor taking into consideration the phenomenon of diffusion in the chemical conversion of these compounds

2. Experimental

2.1 Catalyst synthesis and characterization

A zeolite of type MFI has been modified using the ionic exchanged method, under patent number US 5254327 A, treated with an ammonium sulfate solution 1M ((NH4)2SO4) blending for two hour and reflux system. After, the zeolite was filtered and washed. The sample was dried at 393 K for 12 hours and burned for 5 hours at 973 K.

The modified zeolite showed a specific area of 383 m^2/g reported by BET method, a molar relation Si/Al 37 by ray X fluorescence analysis and <0.5 % w/w in Na concentration determined by ICP.

2.2 Catalytic process

The catalytic cracking process was carried out at laboratory scale. The reactor was constructed of stainless steel with a capacity of 25cc. The operation data was the following: reactions temperatures 773 and 873 K, feed rate 1 cc/min, water rate 0.5 cc/min, space rate 4 h^{-1}, run time 6 h and catalyst load 15 cc.

For a well known of the experimental setup, the process has been divided into three zones: i) zone 1 (Feed): it consists of two (2) glass tanks to store desmineralized water fitted to a connection with inert gas (nitrogen); ii) zone 2 (Reaction): the reactor operates isothermally with an infrared oven and has two wall thermocouples for temperature control; iii) zone 3 (Separation of reactor effluents and receiving liquid product): in the outlet of the reactor system there is a heat exchanger whose cooling stream comes from a cryostat using a mixture of 50% water and 50% ethylene glycol as refrigerant; the cooled reaction product enters in a gas-liquid separator which separates the cracked stream. gas goes to a trap of gases where is collected for a gas chromatograph analysis, finally, the liquid product from the separator is collected in tanks in order to perform a mass balance.

3. Results and discussion

3.1. Kinetic analysis

The experimental data of the catalytic cracking process runs performed at 773 and 873K are shown in Tables I and II.

TABLE I
Catalytic cracking process of pentenes (run at 773 K)

		FEED	PRODUCT	PRODUCT	PRODUCT	PRODUCT	PRODUCT	PRODUCT
SPACE VELOCITY	h⁻¹		4	4	4	4	4	4
VOLUMEN OF CATALYST	cc		15	15	15	15	15	15
SIZE OF PARTICLE	mm		1,20	1,20	1,20	1,20	1,20	1,20
CATALYST STATUS		PENTENES	FRESH	FRESH	FRESH	FRESH	FRESH	FRESH
TEMPERATURE OF CAT BED	°C		500	500	500	500	500	500
TIME OF RUN	h		0,5	1,5	2,5	3,5	4,5	6,0
SYSTEM PRESSURE	atm		1	1	1	1	1	1
FEED FLOW RATE	cc/min		1	1	1	1	1	1
WATER FLOW RATE	cc/min		0,50	0,50	0,50	0,50	0,50	0,50
YEILD	% w/w							
Hydrogen		-	0,000	0,000	0,000	0,000	0,000	0,000
Oxigen		-	0,000	0,000	0,000	0,000	0,000	0,000
Nitrogen		-	0,000	0,000	0,000	0,000	0,000	0,000
CO		-	0,000	0,000	0,000	0,000	0,000	0,000
Acetylene		-	0,000	0,000	0,000	0,000	0,000	0,000
CO2		-	0,000	0,000	0,000	0,000	0,000	0,000
Metane		-	0,301	0,251	0,237	0,199	0,124	0,071
Etane		-	0,501	0,501	0,453	0,396	0,289	0,200
Ethylene		-	6,505	5,804	5,525	4,445	4,456	4,492
Propane		-	1,876	1,256	1,022	0,923	0,848	0,692
Propylene		-	18,303	16,098	15,140	13,580	13,140	13,097
Isobutane		1,75	1,520	1,480	1,356	1,510	1,500	1,535
n-Butane		3,75	3,651	3,077	3,412	3,560	3,370	3,077
i-C4 + n C4		5,50	5,17	4,56	4,77	5,07	4,87	4,61
2-t-Butene		5,48	3,443	3,422	3,013	3,136	3,480	3,672
1-Butene		0,00	3,500	3,646	3,734	3,562	3,758	3,428
Isobutene		1,12	4,585	4,559	4,544	4,572	4,375	4,271
2-c-Butene		4,65	1,236	1,174	1,325	1,580	1,578	1,441
TOTAL C4 Olefins		11,25	12,76	12,80	12,62	12,85	13,19	12,81
n-Pentane		6,10	6,130	6,260	6,140	6,220	6,220	6,240
i-Pentane		45,88	46,599	47,236	47,548	50,526	51,828	50,432
i-C5 + n C5		51,98	52,73	53,50	53,69	56,75	58,05	56,67
3-Methylbutene-1		1,15	0,013	0,061	0,103	0,106	0,119	0,214
Pentene-1		3,14	0,033	0,150	0,261	0,268	0,250	0,543
2-Methylbutene-1		0,35	0,083	0,385	0,653	0,670	0,754	1,352
t-Pentene-2		12,80	0,065	0,303	0,509	0,522	0,588	1,054
c-Pentene-2		2,64	0,035	0,161	0,272	0,280	0,313	0,665
2-Methylbutene-2		0,00	0,156	0,704	1,222	1,251	1,311	2,531
3,3-Dimethylbutene-1		6,06	0,000	0,000	0,000	0,000	0,000	0,000
Cyclopentane		3,50	1,236	3,160	3,051	2,276	1,230	0,661
Cyclopentene		1,62	0,230	0,310	0,480	0,420	0,470	0,331
TOTAL C5 Olefins		31,27	1,85	5,23	6,55	5,79	5,04	7,35
TOTAL		100,00	100,000	100,000	100,000	100,000	100,000	100,000

TABLE II
Catalytic cracking process of pentenes (run at 873 K)

		FEED	PRODUCT	PRODUCT	PRODUCT	PRODUCT	PRODUCT	PRODUCT
SPACE VELOCITY	h⁻¹		4	4	4	4	4	4
VOLUMEN OF CATALYST	cc		15	15	15	15	15	15
SIZE OF PARTICLE	mm		1,20	1,20	1,20	1,20	1,20	1,20
CATALYST STATUS		PENTENES	FRESH	FRESH	FRESH	FRESH	FRESH	FRESH
TEMPERATURE OF CAT BED	°C		600	600	600	600	600	600
TIME OF RUN	h		0,5	1,5	2,5	3,5	4,5	6,0
SYSTEM PRESSURE	atm		1	1	1	1	1	1
FEED FLOW RATE	cc/min		1	1	1	1	1	1
WATER FLOW RATE	cc/min		0,50	0,50	0,50	0,50	0,50	0,50
YEILD	% w/w							
Hidrógeno		-	0,000	0,000	0,000	0,000	0,000	0,000
Oxigeno		-	0,000	0,000	0,000	0,000	0,000	0,000
Nitrógeno		-	0,000	0,000	0,000	0,000	0,000	0,000
CO		-	0,000	0,000	0,000	0,000	0,000	0,000
Acetylen		-	0,000	0,000	0,000	0,000	0,000	0,000
CO2		-	0,000	0,000	0,000	0,000	0,000	0,000
Metane		-	0,300	0,251	0,236	0,198	0,124	0,073
Etane		-	0,499	0,501	0,451	0,394	0,290	0,206
Ethylene		-	6,477	5,802	5,508	4,425	4,460	4,627
Propane		-	1,868	1,256	1,019	0,919	0,848	0,712
Propylene		-	18,224	16,093	15,093	13,518	13,152	13,488
Isobutane		1,746	1,513	1,480	1,352	1,503	1,501	1,581
n-Butane		3,754	3,635	3,076	3,402	3,544	3,373	3,169
i-C4 + n C4		5,500	5,149	4,556	4,754	5,047	4,874	4,750
2-t-Butene		5,481	3,445	3,416	3,370	3,371	3,375	3,374
1-Butene		0,000	3,771	3,740	3,689	3,690	3,695	3,693
Isobutene		1,120	4,589	4,551	4,489	4,490	4,496	4,494
2-c-Butene		4,648	1,585	1,572	1,551	1,551	1,553	1,552
TOTAL C4 Olefins		11,249	13,391	13,279	13,099	13,103	13,119	13,114
n-Pentane		6,098	6,104	6,258	6,121	6,191	6,225	6,426
i-Pentane		45,884	46,398	47,221	47,401	50,295	51,874	51,939
i-C5 + n C5		51,982	52,502	53,480	53,522	56,487	58,099	58,365
3-Methylbutene-1		1,149	0,005	0,045	0,096	0,110	0,114	0,125
Pentene-1		3,141	0,011	0,113	0,242	0,279	0,288	0,315
2-Methylbutene-1		0,347	0,029	0,284	0,605	0,697	0,720	0,787
t-Pentene-2		12,799	0,022	0,221	0,471	0,544	0,562	0,614
c-Pentene-2		2,644	0,012	0,118	0,252	0,291	0,301	0,329
2-Methylbutene-2		0,000	0,054	0,531	1,132	1,305	1,348	1,474
3,3-Dimethylbutene-1		6,062	0,000	0,000	0,000	0,000	0,000	0,000
Cyclopentane		3,504	1,230	3,159	3,042	2,266	1,231	0,681
Cyclopentene		1,623	0,229	0,310	0,479	0,418	0,470	0,341
TOTAL C5 Olefins		31,269	1,592	4,782	6,318	5,910	5,034	4,664
Total		100,000	100,000	100,000	100,000	100,000	100,000	100,000

The behavior of the reaction velocity for ethylene and propylene at 773 and 873 K are shown in Figures 1 and 2, in which can be observed a lineal regression related to concentration of the products. This allows inferring an equation of first order for the reaction kinetics which is consistent with the discussion in the work of Kunzru and Pant, [1], Sedran and de la Puente, [8]. The negligence effect of temperature on the products yield could evidence the role of the diffusion process over reaction rate and its importance for the catalytic process.

This phenomenon could be attributed to the conjunction of catalyst with thermal condition in the process which allows keeping the same reaction rate of the products in the studied

temperatures. Under this focus, Weisz [18] has indicated that the temperature dependence of the reaction and the apparent activation energy could be modified by diffusion effects, supporting the effect that the catalyst design has on the reaction rate in contrast to the temperature.
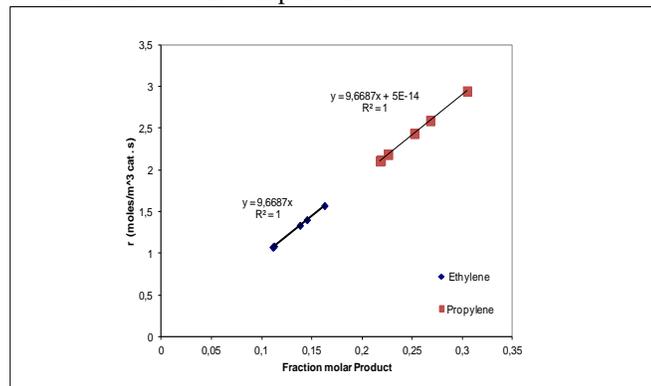

Figure 1. Behaviour of the reaction rate from the catalytic cracking process of pentenes performed at 773 K
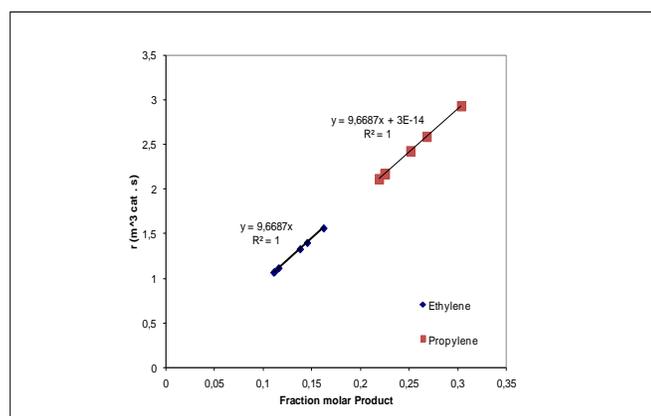

Figure 2. Behaviour of the reaction rate from the catalytic cracking process of pentenes performed at 873 K

3.2 Estimated activation energy
This paper is not addressed to determine the activation energy in each elementary stage of the reaction. Therefore, the focus is showed from the engineer point of view, doing a rough calculation of activation energy based in the Arrhenius correlation at thermal levels for overall reaction. The reaction rates were determined using experimental data where is assumption the combination of reaction rates for the elementary stages with its energy levels.
The obtained value for activation energy was 1.7 kJ.mol^{-1}.
A comparison between the experimental value in this study and the ones reported in the literature on similar processes are shown in Table III; it can be observed a significant reduction in the activation energy. The reduction to one order of magnitude should be the aspect most important that the obtained value. When the activation energies showed in the table III are compared between them, taking in count theirs feeds, catalytic support and calculations methods is noted differences in the energy barriers found by each study, as such has been reported by Redondo [5].

TABLE III
Comparison between values of activation energy

PROCESS		ACTIVATION ENERGY		REF.
DESCRIPTION	CONDITION	VALUE (kJ/MOL)	METHOD	
Catalytic Cracking of Pentene blend	At 773–873K in Modified MFI	1.7	Arrhenius correlation in overall reaction	This Study
Catalytic Cracking of 2methylpentane	In mordenite	6.3	Molecular dynamics simulation	[26]
Catalytic cracking of 2methylbutane	At 296K in ZSM-5	31.9	Quantum chemical calculations	[19]
Pyrolysis in alkyl radicals	High temperature and pressure	126	Canonical variational transition state theory	[11]
Pyrolysis of methylcyclohexane to propylene and ethylene	Atmospheric pressure and (953–1073) K	209	Arrhenius correlation in overall reaction.	[1]
Catalytic Cracking of methylcyclohexane	At 748 - 923K over nano ZSM-5	116	Molecular dynamics simulation	[29]
Catalytic Cracking of methylcyclohexane	At 723 – 783K in Y zeolite	62.8	Arrhenius correlation in overall reaction	[8]
Catalytic cracking of $C_6 - C_8$ olefin isomers	In H-ZSM-5	89	Dispersion corrected density functional theory calculations	[13]

Each method for calculate the activation energy has particulars and limitations, which present an opportunity of interest to organic chemists interested in catalysis at the molecular level, and to surface scientists interested in the nature of physisorbed and chemisorbed states on surfaces in the view of overall chemical process for the engineering area.
The estimated energetic level is consistent with the expected in the research reported by Chen in 2014 [12] , and the magnitude is near with the reported by Sedran and de la Puente [8] and Xiao [19], where can be observed a very small activation energy values for channel size below of 6 Å. For this study it had a molecular diameter of 5 Å (assumed for the pentene), and the channel diameter of the pore in the zeolite was 5.8 Å [19 20, 21]. In this order, the regime for the molecular diffusion in the zeolite pore was called "Configurational" as coined by Weisz in 1973 [22] with which it has associated the "Configurational Activation Energy" attributed to the interactions between the hydrocarbon molecule and the oxygen atoms of the lattice [19]. It is noted that the feed in this study contained compounds C5 $^-$ in this regard the Knudsen regime also was present influencing the decrease of the activation energy in the process. In others words, it is possible to carry out the cracking of pentenes with a lower supply of energy to the process which translates into a

decrease on the operative costs and higher revenues.

Recent Reported work by Shinjiro Fujiyama et al. [23] has shown adsorption of branched hydrocarbon structures on MFI zeolite in the intersection of the zeolite channels, reforcing the theory on beta scission in C-C bond which is most attractive to the zeolite Brönsted protons where the initiation energy is enough for the overall reaction overlapping the energy barriers of the elemental reactions in according to Ken C. Hunter and Allan L. L. East [16] and Joseph A. Swisher et al. [24]. The evidence of no single-file diffusion behavior in the one-dimensional employed MFI zeolites could be the reason of the low activation barriers for the molecular motion causing the molecules not to move in a "hopping-like" motion, as such it has been reported by Schuring [25] where these effects are stronger in the medium-pore zeolites.

3.3 Contributions on catalytic reactors design

The catalytic reactors design has been governed by the knowledge of process information ignoring the technical information of the catalyst. This could be called the "conventional design of catalytic reactors by way of surface chemical".

Now, it could be possible to optimise the design of the catalytic reactor applying the knowledge of the catalyst, for catalytic cracking, which would allow to explore new designs of catalysts resulting in reduction of costs for the construction and operation of the catalytic reactor, and better utilization of physical space in a refinery. This proposal could be called "novel design of catalytic reactors by way of porous chemical".

The conventional design to calculate the tubular reactor volume is based in the following equation:

$$V = F_0 . X / -\upsilon \qquad (1)$$

Where reaction rate is $-\upsilon$, F_o is the feed rate and X is the fraction of the species of interest after conversion.

The proposed design of the tubular reactor will be based in the equation following:

$$S = (\varepsilon L X F_o)/(D c) \qquad (2)$$

Where S is the total catalyst surface, ε is effectiveness factor, L is the effective length travelled by the species within the pore, D is the diffusion coefficient and c is the concentration of the test species.

Thus, the total catalyst surface is estimated, and knowing the surface area and the density of the catalyst, it is possible to obtain the catalyst volume which is roughly reactor volume.

The equation 2 rises from the fundamental assumption of the important role played by the diffusion process for the cracking pentenes combining the mathematical expressions of the kinetic rate, and the diffusion transport rate governed by Fick's first law [26].

From this perspective, it was determined the Thiele Modulus and effectiveness factor to estimate the influence of the diffusion phenomenon on the catalytic cracking of pentenes in modified MFI zeolite using the protocol described in Weisz P. and Hicks [27] and J.F. Marshall and P. Weisz [28] . The found Thiele

modulus was < 0.4 and effectiveness factor equal to 1. This allows to infer a negligence influence of pore diffusion resistant in the studied kinetic regime under the process condition. These results are in agreement with the reported by Konno et al. [29] and Xiao [19]. The diffusion constant, Table IV, was determined using the calculation method proposed by J.F. Marshall & Paul Weisz [28].

Based in the results of the activation energy and difusional effect above mentioned, the intention is to show the impact on the catalytic reactor design when the diffusion process is favored and takes an important role on the chemical reaction. For this, it shows in the table IV technical data for the calculation of catalytic reactor volume.

TABLE IV
Technical data related to catalytic cracking of pentenes

TECHNICAL DATA	VALUE	SEARCH
Molar fraction of propylene	0.2181	a
Flow rate of feed, cc/min	1	a
Feed density, g/cc	0.61	a
Reaction velocity of propylene, $mol_{propylene}/m^3_{cat}.s$	2.1085	a
Efficiency of catalyst	1	b
Catalyst diameter, mm	1.2	a
Diffusion coefficient, 10^{-15} m^2/s	2	b
Concentration of propylene, %p/p	13	a
Specific surface of catalyst, m^2/g	383	a
Catalyst density, g/cc	0.539	a

a. Experimental data from this study. b. Estimated value for this study.

Handling the equation 1 with the data from Table IV was possible to estimate the catalyst volume obtaining a value of 15 cc coinciding with the real one. In same manner, it was handling the equation 2 obtaining a value of 13 cc, evidencing a reduction of 15% in the catalyst volume when difusional phenomena are considered. In industrial level, this could be more than 15% in the reactor volume and over 20% on saving in construction cost. These results open the opportunity to explore new designs of catalysts where intrinsic reactivity, diffusion transport and physics parameters of catalyst play an important role in the reaction kinetic and reactor design which could allow a reduction in the reactor volume and supplied energy to process.

4. Conclusions

The activation energy of the catalytic cracking of the pentenes was calculated obtaining a significantly reduction in comparison to reported in the literature. It was proposed a mathematical model for the design of tubular reactors $S = (\varepsilon L X F_o)/(D c)$ where the phenomenon of diffusion is considered important as such the catalyst technical data obtaining a significant reduction in the estimated volume of reactor.

5. Acknowledgment

6. References

i.   Kunzru D., Pant K. Chem. Eng. J., 63 (1997) 123-129
ii.   Franz J., Camaioni D., Autrey T., linchan J., Alnajjar M. (2000). J. Anal. Appl. Pyrol 54 (2000) 37-64
iii.   Ranzi E., Dente M., Pierucci S., Biardi G. Ind. Eng. Chem. Fundam, 22 (1983) 132-139
iv.   Belohlav Z., Zamostny P., Herink T.. Chem Eng Proc 42 (2003) 461-473
v.   Redondo A., Jeffrey P., Guo.Y. (1999). Catal. Today 50 (1999) 517-523.
vi.   Chen J., Bozzano A., Glover B., Fuglerud T., Kvisle S. (2005). Catal. Today 106 (2005) 103-107.
vii.   Bortnovsky O., Sazama P., Wichterlova B., Appl. Catal A: General 287 (2005) 203-213.
viii.   Sedran U., de la Puente G. Appl. Catal. A. General 144 (1996) 147-158.
ix.   Marshall, J., Weisz P. J. Catal. 111 (1988) 460-463
x.   Rodríguez A., Grande C., Cavenati S., Barcia P., Hammer J., Fritz H. Chem. Eng. Sci. 61 (2006) 3053-3067.
xi.   Ratkiewicz, A. Phys. Chem. Chem. Phys.,13 (2011) 15037-15046
xii.   Chen, C. , Rangarajan S. , Hill I.M. and Bhan, A. ACS Catal., 4 (7) 2014, 2319–2327
xiii.   Mazar M. N. , Al-Hashimi S., Cococcioni M.and Bhan, A., J. Phys. Chem. C, 117 (45), 2013, 23609–23620
xiv.   Frash, M. V. , Kazansky ,V. B. , Rigby, A. M. and van Santen, R. A. J. Phys. Chem. B, 102 (12), 1998, 2232–2238

xv.   Li, Q., and East, A. L.L., Can. J. Chem. 83, 2005, 1146–1157
xvi.   Hunter, K. C., and East, A. L. L., J. Phys. Chem. A 106, 2002, , 1346-1356
xvii.   Kärger J., Vasenkov S. (2005). Microporous and Mesoporous Materials 85. 195-206
xviii. Weisz P. Chem eng proc symp series 25, volume 55 (1959) 29-36
xix.   Xioa J. (1990). The diffusion mechanism of hydrocarbons in zeolites. PhD Thesis. Massachutts Institute of Technology
xx.   Xioa J., Wei J. (1992). Chem. Eng. Sci. 47 (1992) 1123-1141
xxi.   Xioa J., Wei J. (1992). Chem. Eng. Sci. 47 (1992) 1143-1159
xxii.   Weisz P.B. CHEMTECH 3. (1973). 498
xxiii. Fujiyama S., Seino S., Kamiya N. , Nishi K. , Yoza K. and Yokomori Y. Phys. Chem. Chem. Phys., 16, 2014, 15839-15845
xxiv.   Swisher, J. A., Hansen, N., Maesen, T., Keil, F.J., Smit, B..,and Bell, A. T. J. Phys. Chem. C 114, 2010, 10229–10239
xxv.   Schuring, D., Jansen, A. P., van Santen, R. J. Phys. Chem. B., 104:5 (2000) 941-948
xxvi.   Buyevskaya O., Wolf D., Baerns M. Catal. Today 62 (2000) 91-99.
xxvii. Weisz P. & Hicks J. Chem Eng Sci. 17 (1962). 265-275
xxviii. Marshall, J.F. and Weisz, P. B: Journal of Catalysis 111, 1988, 460-463
xxix.   Konno H.,   Ohnaka R. , Nishimura J., Nakasaka Y. Tago T. and Masuda T. Catal. Sci. Technol., 4, 2014, 4265-4273