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Study Of Bioethanol Conversion in Aliphatic Hydrocarbons on Zeolite Catalysts

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Abstract

Bioethanol conversion has been studied on zeolite catalysts ZSM-5 type, simple and modified by impregnation with hydrogenating function metals. The study carried on in micropilot laboratory installation in catalyst fixed bed. Operation conditions were: temperature range 350-450°C, pressure range 1-50 bar, hourly space velocities range for ethanol 0.5-2 h^{-1}. The reaction carried on in nitrogen inert atmosphere and in the presence of hydrogen. Reaction products were collected as gaseous fraction and analyzed by gas-chromatography to establish the composition as C_1-C_4 fraction, alkanes and alkenes. It was emphasized the influence of operating parameters catalysts type on C_1-C_4 compounds distribution in gaseous products.

Key words: *bioethanol, zeolite catalysts, Pd-ZSM-5, C_1-C_4 aliphatic hydrocarbons*

Introduction

Currently, on international plan, there are studies and documentations concerning the conversion of ethanol on catalysts supported iron by different methods. ZSM5 zeolite catalysts impregnated iron develops the suitable achievements on the conversion of ethanol in liquid or gaseous hydrocarbons, preferably, aromatics [1]. Relevant yields of C_3-C_4 fractions have emphasized in the conversion of ethanol on HZSM-5 zeolite catalyst [2]. The results show the significant amounts of propylene in the case of aluminum impregnated on the ZSM5 catalysts [3]. The influence of metals such as, Zn and Ga on the ZSM-5 catalysts during the conversion process of ethanol towards aromatic hydrocarbons was significant [4, 5]. The effect of ionic exchange between the zeolite catalyst and alkali metals (Li, Na, K), alkaline earth metals (Mg, Ca, Sr, Ba) and transition metals (La, Ce, Cr, Mn, Co, Ni, Pd, Cu) determine the important yields on C_3, olefins and aromatics, but with selectivities as function of the exchange cation nature [6]. Knowing the ethanol like as renewable source of oils, olefins and aromatics, because it is derived from biomass, that is converted into gaseous fractions on zeolite catalysts containing Fe, Zn, Ga, Al metals by ionic exchange.

On the national plan, there are studies regarding the zeolite catalysts in different conversion reactions of aliphatic hydrocarbons into aromatics [7-9], the methanol conversion into gasoline [10] and the conversion of bioethanol into light hydrocarbons [11]. In this study, the focus is to obtain a high yield of gaseous fraction with C_3-C_4 alkanes hydrocarbons by the selective

catalytic systems, such as zeolitic systems and modified by ionic exchange with different metals types.

Experimental studies on testing of catalysts for bioethanol conversion

As a result of literature study, H-ZSM-5 and Pd-ZSM-5 catalysts were chosen for experiments. The testing of these catalysts carried out on a micropilot plant in continuous system and fixed catalytic bed (Figure 1).

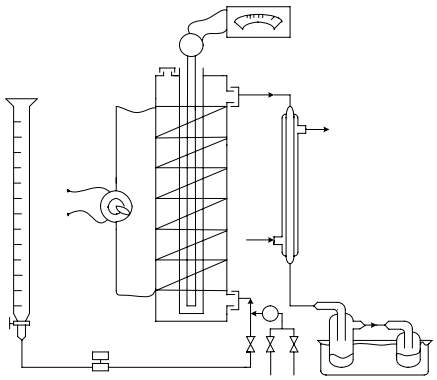


Figure 1. Laboratory micropilot for bioethanol conversion

Experimental plant description

The micropilot main component is a reactor having the following features: maximum pressure 80 bar; maximum temperature 600^{O}C, maximum feed flow with liquid product: 600cm^3/h, maximum flow of exhaust gas 3500 N l /h.

The plant has: the tubular reactor; the coolers with indirect contact; vertical gas-liquid separator; rotameter for measuring the flow of exhaust gas phase separated by reaction; gas meter for measuring the volume of exhaust gas from the separator, the pressure reducer for regulation the pressure on the system.

The plant has a system that ensures: the adjusting control of temperature reactor, the indication of the feed pressure; the coupling of heating system.

The feed of liquid reactants carry on in a measuring burette and the feed of gaseous reactants carry on from gas cylinders with pressure reducer.

The heating of reactants is done electrically, in the upper region of the synthesis reactor, the plant not being provided with the preheating systems of them.

The cooling of effluents is done with water from the drinking water network, by both indirect contact in the cooler provided at bottom of reactor and the separator, also provided with the cooling coating. The exhaust of incondensable products in separator vessel is achieved with a valve located upstream of rotameter and gas meter.

The adjusting of the temperature in the both two regions of the reactor is done automatically. In order to avoid the change of current direction of reactant flow, so the feed gaseous route of hydrogen and liquid route are provided with safety valves.

Experimental program

The achievement of standard tests for catalysts based on ionic exchange requires an operation of synthesis plant for a period that allows the catalyst to be in steady operation. As result of some preliminary tests has been established that the use of an inert as glass or spherical ceramic material with 2.5, respectively 5 mm size in ratio 2:1 provides an efficient preheating for specific operating conditions of the experiment, allowing the use of maximum volume of 10 cm^3 catalyst. The region located under catalytic bed close to the bottom of the flange is also filled with granular inert having the same size.

Experimental tests focused on ZSM-5 catalyst modified to acid form, binded in the presence of alumina and impregnated with 0.7% wt Pd was the study of the influence of following parameters:

- The influence of operating temperature on the bioethanol conversion in different reaction products. T
- The influence of operating pressure on reaction products distribution.
- The influence of reduced palladium to metallic form on the hydrogenated activity of olefin type compounds from the effluent of bioethanol conversion.

In this study was used ethanol as raw material provided by the SC SILAR TRADING SRL and hydrogen cylinder from LINDE, purity 99.99%.

As a result of the cooling processing and condensation of liquid phase, the reaction products were in gaseous phase. The analysis of gaseous products was done on a CARLO ERBA INSTRUMENTS HRGC MEGA-SERIES 5300 gas chromatograph with a stainless steel column of 1 with inner diameter of 4 mm and the height of 6 m, with 20 % β, β – diizopropionitryle as a stationary phase. The detector of chromatograph was catarometer (based on thermal conductivity) and the analytical data was collected and analyzed with a specialized software Chrom-Card. The analytical results were presented in the percentage of area equivalent to volumetric or molar percent. The carrier gas was helium from LINDE.

Results and Discussions

The catalysts have been tested function of textural and morphological characteristics. The textural, acidity determinations, respectively XRD analyses have been obtained (Table 1 and Figure 2).

Table 1. Textural characterisctics and total acidity for H-ZSM-5 zeolite catalyst

Characteristic property	Value
Silica/alumina molar ratio	40
Specific area, m^2/gr	208
Pore volume, cm^3/gr	0,217
Distribution of pore volume, % 0-25 A 25-50 A 50-100 A 100-300 A	 58,54 28,39 8,5 4,57
Total acidity, mechiv/gr	0,38

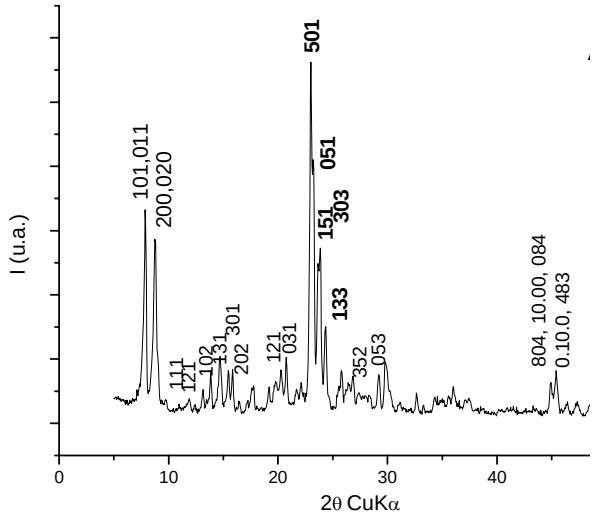


Figura 2. XRD patterns of ZSM-5 zeolite catalysts

It is expected that the inferior alcohols such are methanol and the ethanol, in the presence of zeolite catalysts acid form, as fresh catalysts or modified with the different metals, can lead to different hydrocarbons, especially olefins and aromatics, with the different number of carbon atoms, but the size of chain being limited to the chain specific for the gasoline fraction.

The main reaction of ethanol it is expected to be a dehydration reaction by carbocationic mechanism (meaning the reaction of elimination), obtaining ethylene and water, in the presence of acid catalysts such are H-ZSM-5 catalysts at 200-300°C temperature.

Pd-ZSM-5 catalyst (0.7% Pd)

This study was focused on the dehydration reaction, most important should be the reactions of chain growing, obtaining C_3 and C_4 hydrocarbons. These reactions with olefins obtaining are expected to be followed by hydrogenation reactions due to addition of 0.7% wt palladium on zeolite catalyst and the presence of hydrogen in the reaction flow. There are suspicions regarding the hydrogenating activity of metallic palladium when the product reaction contains water (water resulted from ethanol dehydration), which can inhibit the hydrogenating action of platinum metals.

In this context, it was studied the effect of operating conditions (temperature and pressure) on the main reactions (the dehydration, chain increasing, olefins hydrogenation) at constant space velocity. The ethanol/hydrogen molar ratio was constant for all experiments. From the data presented in table 2 and the figures 1-6 it could be established qualitatively and in some measure quantitatively, the effect of reaction temperature and pressure on the reaction products distribution, in % volume of component from gaseous product.

We will consider only the gas product, due to the formation only of small amounts of liquid products. The experiments have been conducted regarding the catalytic conversion of ethanol on ZSM-5/alumina catalyst impregnated with 0.7 %wt Pd at three temperatures and two pressures, maintaining the space velocity and ethanol/hydrogen ratio constant. Using hydrogen in these experiments, the aim was to lead the distribution of reaction products from olefins to alkanes.

In Table 2 there are presented the operating parameters and gaseous composition of the reaction product resulted to catalytic conversion of ethanol in the presence of hydrogen, on ZSM-5/ γ-alumina catalyst impregnated with 0.7 % wt Pt at $\omega = 2\ h^{-1}$ and the ethanol/H_2 constant molar ratio.

Tabel 2. Reaction product composition (in %volume) from the catalytic conversion of bioethanol on ZSM-5 zeolite catalyst impregnated with 0.7% wt Pd

P= 10 bar, ω=2h^{-1}													
Temp	**Gaseous product composition (%vol)**												
	H_2+C_1	C_2	C_2'	C_3	C_3'	iC_4	nC_4	1+iC_4^-	$2C_4^-$ trans	$2C_4^-$ cis	C_4^-	ΣC_5^-	ΣC_4^-
370 ^{0}C	35,48	13,65	44,45	-	4,24	0,89	0,39	0,19	0,18	0,29	-	0,19	1,96
400 ^{0}C	17,71	15,75	56,82	-	4,85	0,50	0,50	0,59	-	0,59	-	4,00	2,20
420 ^{0}C	24,50	11,53	59,26	-	3,43	-	-	-	-	-	-	0,86	-
P= 20 bar, ω=2h^{-1}													
370 ^{0}C	26,58	42,07	19,90	3,40	6,15	0,33	0,44	0,65	-	0,84	-	0,79	2,26
400 ^{0}C	30,45	38,45	26,96	3,08	4,67	-	0,52	0,72	-	-	-	0,76	1,24
420 ^{0}C	8,06	42,71	35,77	3,15	6,87	-	0,50	0,76	-	1,31	-	0,83	2,58

As mentioned above, the inferior alcohols such as the methanol and the ethanol, in presence of zeolite catalysts in the acidic form or modified with various metals, can lead to the different hydrocarbons such are olefins and aromatics, with variable number of carbon atoms, but the size of catena being limited to the fraction of gasoline. In presence of the H-ZSM-5 acid catalysts at 200-300°C, the main standard reaction will be the dehydration reaction by carbocationic mechanism, with water elimination and ethylene production.

The dehydration reaction and the chain growth reaction to C_3 and C_4 hydrocarbons have followed. Beside these reactions with obtaining of olefins, was followed the potential presence of the hydrogenation reaction due to addition of 0.7 % wt. palladium and the hydrogen presence in the reaction flow. The hydrogenation activity of palladium could be inhibited when the reaction product contains water from ethanol dehydration.

In this context, the effect of operating parameters, the temperature and the pressure on the main reactions (such as the dehydration, the chain growing, and the hydrogenation of the different olefins from reaction product) at the constant space velocity speed and the ethanol/ hydrogen molar ratio have followed. The data presented in the table 1 and the figures 1-6 show the temperature and pressure effect on the distribution of reaction products, in % volume of the component from gaseous product.

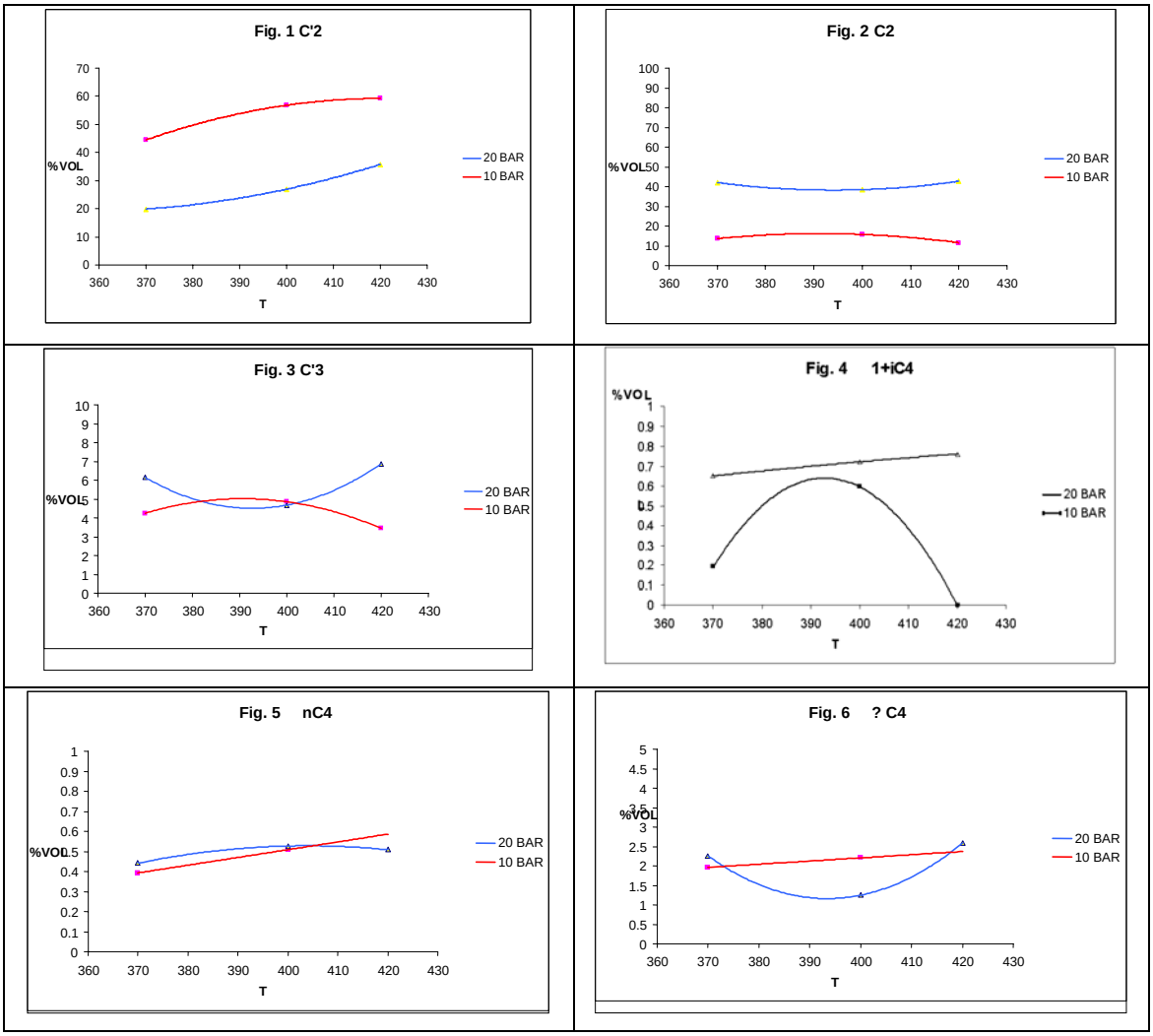
Thus, the data from the Table 2 and the Figures 1 and 2 offer informations about the catalyst effect and the influence of operating parameters, such are temperature and pressure, on the main dehydration product of ethanol-ethylene and on the hydrogenation product – ethane. It could be observed that ethylene obtaining is favored by the slowly increase of the temperature and pressure increasing, the C_3 product composition being up to 10% in the favorable operating conditions.

Regarding the formation of hydrocarbonated product with four atoms of carbon, in figures 4, 5 and 6 could be observed that the percentage of i-C_4 and n-C_4 hydrocarbons is about the same order (~ 0.5 % vol), and variation with the temperature and the pressure is not significant. The figure 6 shows that the percentage of C_4 total fraction (olefins and paraffins) is about 2-3% volume, increasing slowly with the temperature and being slowly influenced by the pressure increasing.

Finally, the catalyst has a strong dehydration and hydrogenation effect and also a significant effect of the hydrocarbonated chain increasing up to 15-20% volume. To emphasize this effect of chain increasing, researches will be focused on the added metal type.

Temperature reaction is higher (370-420°C) at 10 bar pressure and lower at 20 bar pressure. Ethane concentration variation is related to temperature variation, and ethane concentrations are two times higher at 20 bar comparing with concentrations obtained at 10 bars.

ZSM-5/alumina catalyst impregnated with 0.7% wt Pd has an important hydrogenated activity in presence of the hydrogen; this activity isn't inhibited by the presence of water from dehydration. Regarding the growing of hydrocarbonated chain reaction, it could be observed, according to Figure 3 and Table 1, a significant amount of propylene at 10 bar pressure in the presence of this catalyst. Only on pressures higher than 20 bar propane composition is around 3%, representing about half of the propylene amount. This conversion leads to reaction products with higher hydrocarbonated chain comparing to the raw material.



H-ZSM-5 catalyst

Table 3. Operating conditions and composition of gaseous product at the bioethanol conversion on H-ZSM-5 catalyst, pressure 4 bar and V_{ZR}= 40 cm^3

Gaseous product composition	% vol									
T,^{0}C, ω,h^{-1}, eluent	C_1	C_2	C_2'	C_3	C_3'	iC_4	nC_4	$1+iC_4$	trans C_4^{2-}	cis C_4^{2-}
430, 1, N_2	28,29	0,53	50,87	2,48	3,65	4,59	1,22	2,09	3,24	1,11
450, 0,5, N_2	29,28	1,55	29,73	7,61	18,69	3,59	2,08	4,47	2,99	-
420, 0,5, H_2	18,89	3,95	37,82	5,74	9,39	4,08	3,67	6,89	4,91	3,66
*380, 0,5, H_2	26,57	18,84	46,48	4,88	0,89	0,36	0,8	1,23	-	-

** The experiment carried out at 50 bar pressure*

The experiments that carried out on H-ZSM-5 catalyst at temperatures of 430-450°C, in nitrogen flow, lead to important amounts of ethylene compared to C_3 and C_4 fraction. The bioethanol conversion into C_3 and C_4 fraction is not significantly influenced by the nature of the feeding gas (nitrogen and hydrogen) as a dilution agent. The increase of pressure to 50 bar is unfavorable to obtain the reaction products with higher of hydrocarbonated chain.

Conclusions

- The experiments have been carried out on H-ZSM-5, Pd-ZSM-5 catalysts
- Raw material was ethanol with 5% water content;
- The catalysts were prepared in ZECASIN laboratories;
- Operating conditions were: 350 - 450ºC temperatures and the space velocities 1 and 1.5 h^{-1};
- Experiments duration was about one hour;
- After each experimental test the catalyst has been regenerated;
- The results for the same experimental conditions are:

Modified catalyst	Unmodified catalyst
• Conversion – over 99% ; • PBI selectivity– over 22%; • PBI yield -12%;	• conversion – over 99%; • PBI selectivity -36%; • PBI yield – 19%

- H-ZSM-5 catalyst showed best activities for bioethanol conversion.

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Studiul conversiei bioetanolului în hidrocarburi alifatice pe catalizatori zeolitici

Rezumat

Conversia bioetanolului a fost studiată pe catalizatori zeolitici de tipul ZSM-5, simpli şi modificaţi prin impregnare cu metale cu funcţie hidrogenantă. Experimentele au fost efectuate pe o instalaţie micropilot cu catalizator în pat fix. Condiţiile de operare au fost: temperaturi cuprinse între 350-450°C, presiuni cuprinse între 1-50 bar, viteze volumare pentru etanol 0,5-2 h^{-1}. Reacţiile au avut loc în atmosferă inertă de azot şi în prezenţa hidrogenului. Produşii de reacţie au fost colectaţi ca fracţie gazoasă şi analizaţi gaz-cromatografic pentru a stabili compoziţia fracţiilor C_1-C_4 (ca alcani şi alchene). A fost evidenţiată influenţa condiţiilor de operare şi a tipului de catalizator asupra distribuţiei produşilor de reacţie gazoşi.