Alkylation of Benzene with Bioethanol on Modified Zeolitic Catalyst

ANCA GABRIELA PARCIULEA[1]*, GHEORGHE HUBCA[2], CORNELIU CINCU[2]
[1] Ministry of Education, 28-30 General Berthelot Str., 010168, Bucharest, Romania
[2] University Politechnica of Bucharest, Faculty of Applied Chemistry and Materials Science, 149 Calea Victoriei Str., 010072 Bucharest, Romania

Alkylation of benzene with bioethanol (95% and 100% concentration) has been done in a laboratory tubular reactor using a new modified zeolitic catalyst. The alkylation experiments have been done at different reaction temperatures , pressures and benzene/bioetanol molar ratio in order to establish their influence on the final composition of the reaction product, selectivity and conversion. The feed and products are analysed by gas chromatography. There was small differences between 100% bioethanol and 95% bioethanol aqueous solution in experimental alkylation results that it possible to use 95% bioethanol solution as alkylating agent

.Keywords: alkylation benzene, bioethanol, ethylbenzene, zeolitic catalyst

The alkylation of aromatic compounds is widely used in synthesis of petrochemical products fine chemicals and intermediates [1-4].

At the present approximately 90% of ethylbenzene (EB) production a raw material for manufacturing of styrene and polystirene is obtained by acid catalysed alkylation of benzene with ethylene using Friedel Craft catalyst ($AlCl_3$). The environmental and corosion problems associated with Friedel Crafts catalyst are eliminated with the use of zeolitic catalysts. The vapour phase alkylation of benzene with etylene in the presence of ZSM-5 zeolites is a comercial method for the synthesis of EB (the Mobil Badger Process [5, 6].

Different types of zeolite catalysts such as ZSM-5[7, 8, 16], $Alcl_{3,}$ 13X and HY[9] were investigated and their advantages were demonstrated [10].

The ethylene, a petrochemical product, can be substituted by ethanol in alkylation process of benzene, toluene, or diethylbenzene and the results have been reported earlier [3, 9, 11, 12].

As the ethanol can be obtained in the fermentation process of carbohydrates derived from biomass (named bioetanol (BE), the alkylation of benzene with bioethanol became an interesting way in chemical industry .

In order to avoid the energy consumption in the isolation of pure ethanol by complex process (azeotropic distillation) from fermentation mixture , the use of zeolitic catalyst gives the possibility of benzene alkylation with an aqueous bioethanol solution instead of pure ethanol [13]. The presence of water will not cause any catalyst deactivation [1, 14].

In this paper the alkylation of benzene with bioethanol has been carried out in a laboratory metallic continuous flow reactor. The main purpose of this work is to establish the activity of this new zeolitic catalyst and the influence of experimental conditions (temperature, pressure, molar ratio benzene/ethanol) on the final composition of the reaction product and catalyst selectivity.

Experimental part

Materials, equipment and materials

All reactants were high purity reagents (pure ethanol, Ni–acetate, Ce $(NO_3)_{4,}$ 95% aqueous ethanol solution is obtained by distillation of fermentation mixture of carbohidrates derived from biomass (distillation temperature 78,15°C at 1 barr) [15]. The catalyst utilized in this study was obtained from the comercial zeolite ZSM-5 ($SiO_2/Al\ _2O_3=100$) in the hidrogen form, from EKA Chemicals. The chemical modification of the zeolite was achived by agitating for 24 h a mixture in excess of aqueous solution 0.1M, Ni acetate and 0.1 M Ce $(NO_3)_4$(molar ratio Ni acetate /Ce $(\ NO)_3=1/1$) with ZSM-5 zeolite .

The wet zeolite was dried and then activated by calcining at 450°C for one hour. A mixture of the modified zeolite and silica powder (0.25-0.30 mm particles size) was used as catalyst in the alkylation reactor. Atomic mass spectroscopy analysis of modified catalyst gives the following concentrations for Ni=7.8% and Ce =8%.

Alkylation reactor

The catalytic experiment were carried out in a fixed bed of continuous down flow cylindrical stainless steel reactor (ID=0.02m. length =0.5 m) electrically heated and followed by a condenser and a collector (fig 1).

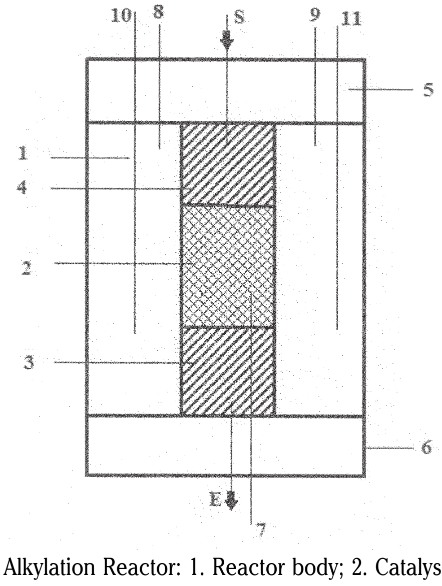

Fig. 1. Alkylation Reactor: 1. Reactor body; 2. Catalyst zone; 3-4 Inert zone; 5-6 Flanges; 7-11 thermocouples; S – reactant mixture supply; E – exit of reaction products

---

* *email.: parciuleaanca@yahoo.com; Tel.: 021 4022703*

Experimental procedure

The reactor was changed with glass spheres an inert bed of (2-3 mm diameter) (height occupied =0.16 m)and then with catalyst 50 cm^{3}of catalyst which occcupied ~0.100 m height of the reactor. Finally the reactor was filled with glass spheres and then electrically heated at high temperature, between 300 -450^{0}C (controlled temperature in three zones: catalyst and inert bed).

The benzene/ethanol mixture in desired molar ratio 1/1, 2/1 was introduced using metering pump (Model Eldex , Optos Metering Pump, PN 5982) on the top of the reactor and vaporized in the first inert zone with glass spheres . The nitrogen was used as carrier gas (4-10 mL /min).

The desired pressure in the reactor (1-40 bar) was adjusted with the help of a needle valve and read on the pressure gauge.

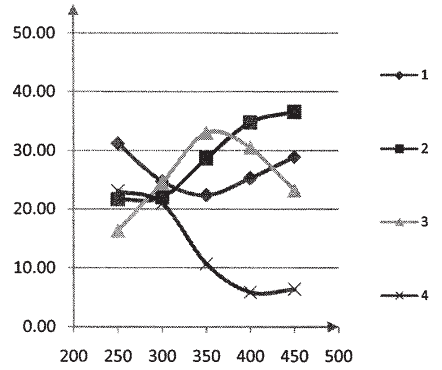

Fig. 2. Chemical composition of the alkylation product as a function of temperature; benzene/ethanol. (100%)=1/1(mole/mole) 1-benzene, 2-ethylbenzene, 3-diethylbenzene, 4 –xilene, trimethylbenzene, methylbenzene

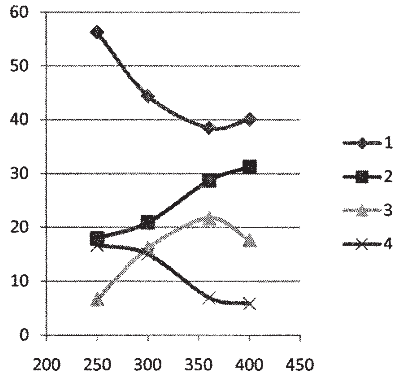

Fig. 3. Chemical composition of the alkylation product as a function of temperature;benzene/ethanol.(100%)= 2/1(mole/mole) 1-benzene, 2-ethylbenzene, 3-diethylbenzene, 4 -xilene, trimethylbenzene, methylbenzene

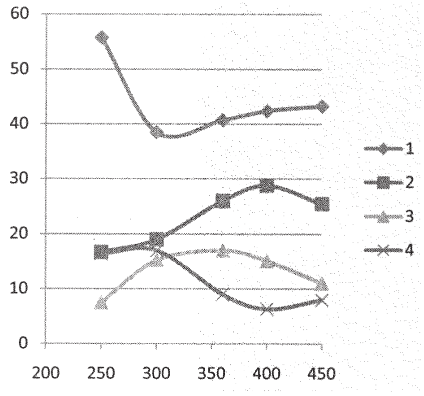

Fig. 4. Chemical composition of the alkylation product as a function of temperature; benzene/ethanol. (100%)=3/1(mole/mole) 1-benzene, 2-ethylbenzene, 3-diethylbenzene, 4 -xilene, trimethylbenzene, methylbenzene

The product vapour and unreacted reactants were condensed in the condenser and the liquid samples collected were analysed by gas chromatography (VARIAN CP 3800) using a column WCOFUSED Silica 30 mx 0.52 mm.

Results and discussions

The main reaction products used in this alkylation process are ethylbenzene and dietylbenzene as subproduct, so we will judge the process function of these chemicals.

Chemical composition of the alkylation product as a function of reactants ratio benzene/bioethanol) is presented in tables 1, table 2 and figures 2-7.

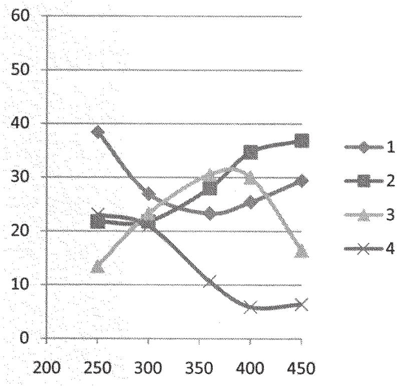

Fig. 5. Chemical composition of the alkylation product as a function of temperature; benzene/ethanol. (96%)=1/1(mole/mole) 1-benzene, 2-ethylbenzene, 3-diethylbenzene, 4 -xilene, trimethylbenzene, methylbenzene

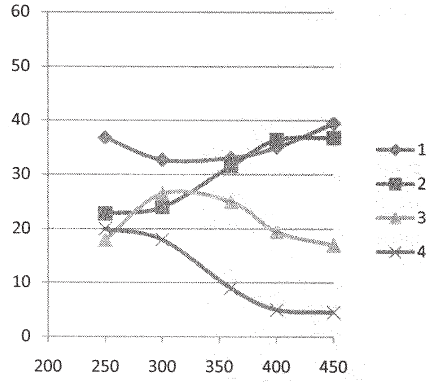

Fig. 6. Chemical composition of the alkylation product as a function of temperature; benzene/ethanol. (96%)=2/1(mole/mole) 1-benzene, 2-ethylbenzene, 3-diethylbenzene, 4 -xilene, trimethylbenzene, methylbenzene

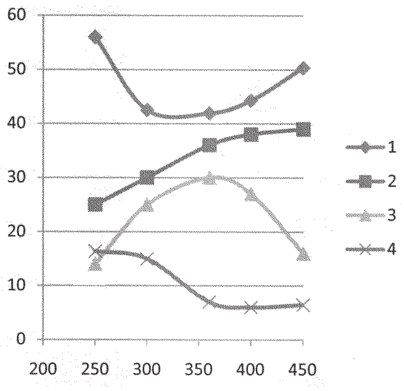

Fig. 7. Chemical composition of the alkylation product as a function of temperature; benzene/ethanol. (96%)=3/1(mole/mole) 1-benzene, 2-ethylbenzene, 3-diethylbenzene, 4 –xilene, trimethylbenzene, methylbenzene

Molar ratio Benzene/ ethanol	Temperature, t^0C	Number of the test	Composition (%)						
			Light components	Benzene	Toluene	Ethylbenzene	X, TMB, MEB	Diethylbenzene	Heavy Compo -nents
1/1	250	17	0.04	31.20	0.30	21.70	23.10	16.30	7.30
	300	18	0.20	24.80	0.50	22.00	21.00	24.50	6.70
	360	19	0.20	22.40	0.90	28.70	10.70	33.00	4.30
	400	20	0.10	25.30	0.90	34.80	5.90	30.50	2.60
	450	21	0.30	29.00	1.70	36.60	6.40	23.20	2.90
2/1	235	22	0.50	52.70	0.40	20.90	14.00	8.70	2.60
	240	23	0.40	55.30	0.30	18.10	17.60	6.30	2.10
	250	24	0.20	56.30	0.30	17.90	16.70	6.70	1.90
	300	25	0.30	44.40	0.60	20.90	15.00	16.10	2.70
	360	26	0.20	38.50	1.00	28.70	7.00	21.70	2.90
	400	27	0.30	40.10	1.70	31.30	5.90	17.60	3.30
3/1	250	28	1.10	55.80	0.20	16.70	16.40	7.50	2.30
	300	29	1.10	38.50	0.90	19.00	17.00	18.00	6.00
	360	30	0.70	40.70	2.00	26.00	9.00	15.20	4.40
	400	31	0.70	42.40	3.00	28.80	6.30	15.10	3.70
	450	32	1.50	43.30	5.00	25.50	8.00	11.00	6.00

Table1
CHEMICAL COMPOSITION OF THE ALKYLATION PRODUCT AS A FUNCTION OF BENZENE/BIOETHANOL RATIO AT DIFFERENT TEMPERATURES (Et OH =100%, p=2 BARR, VOLUMETRIC INPUT OF THE REACTANTS 25 mL/min, NITROGEN INPUT=2L/h)

TMB - trimethylbenzene
MB - methylbenzene
X - other products

Molar ratio Benzene /ethanol	Tempera ture ^0C	test	Composition (%)						
			Light components	Benzene	Toluene	Ethylbenz-ene	X, TMB, MB	Diethylbenze -ne	Heavy Compo -nents
1/1	250	17	0.10	38.40	0.40	21.75	23.10	13.50	4.50
	300	18	0.40	26.90	0.60	21.80	21.00	23.30	6.25
	360	19	0.40	23.30	1.10	28.00	10.70	30.50	4.70
	400	20	0.20	25.40	1.20	34.70	5.90	30.00	2.60
	450	21	0.30	29.40	1.50	36.90	6.40	16.50	2.50
2/1	250	22	0.50	36.80	0.40	22.80	14.00	23.90	4.50
	300	23	0.40	32.70	0.40	24.40	17.60	28.50	3.70
	340	24	0.20	33.10	0.50	31.60	16.70	23.00	1.60
	400	25	0.30	36.80	0.50	36.40	15.00	17.70	0.90
	450	26	0.20	39.50	0.60	36.80	7.00	10.15	1.50
3/1	250	28	1.10	52.70	0.15	20.10	16.40	21.00	2.00
	300	29	1.10	40.50	0.40	24.00	17.00	23.90	2.30
	350	30	0.70	39.90	0.40	30.70	9.00	15.20	1.10
	400	31	0.70	42.30	0.40	34.10	6.30	15.10	1.00
	450	32	1.50	48.40	0.60	34.10	8.00	11.00	1.00

Table2
CHEMICAL COMPOSITION OF THE ALKYLATION PRODUCT AS A FUNCTION OF BENZENE/ BIOETHANOL RATIO AT DIFFERENT TEMPERATURES (Et OH =96%, p=2BARR, VOLUMETRIC INPUT OF THE REACTANTS 25 mL/min, NITROGEN INPUT=2L/h)

TMB - trimethylbenzene
MB - methylbenzene
X - other products

The experimental at different temperatures, data presented show that the optimum value for the ratio benzene/ethanol in 2/1 (mole/mole) . The small content in ethylbenzene (EB) for the ratio benzene/bioethanol=3/1 is not important because diethylbenzene (DEB) will be converted into EB in an subsequent process (transalkylation).

Atomic mass analysis spectroscopy of the modified catalyst gives the folowing concentration presented in the tables 1 and 2.

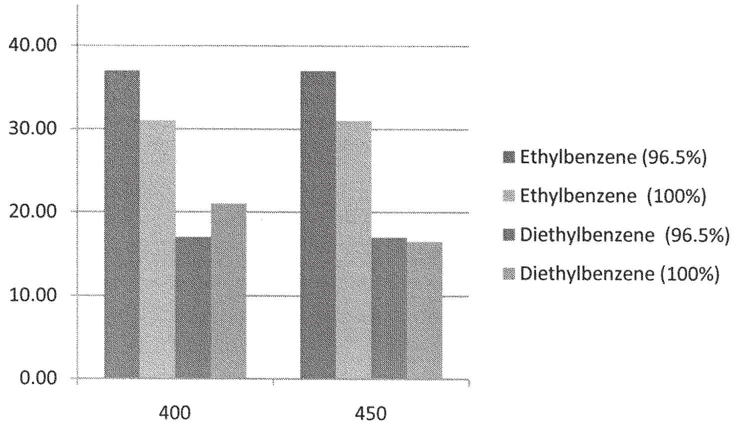

Fig 8. Chemical composition of the alkylation product (%) as a function of the ethanol concentration (100% and 96,5%) at 400^{0}C and 450^{o}C, benzene/ethanol=2/1 (mole/mole).

Table 3
CHEMICAL COMPOSITION OF THE ALKYLATION PRODUCT AS A FUNCTION OF THE PRESSURE T=350 ^{0}C, BENZENE/ ETHANOL 100%=2/1(mole/mole) VOLUMETRIC INPUT OF THE REACTANTS =2.5 mL/min , INERT GAS (NITROGEN) INPUT 2L/h

Pressure bar	Number of the test	Composition %						
		Light components	Benzene	Toluene	Ethylbenzene	X, TMB, MB	Diethylben -zene	Heavy Compo -nents
2	0P	0.04	38.90	0.40	30.70	4.90	23.90	1.10
20	1P	0.00	28.00	0.30	31.30	4.40	34.00	1.90
25	2P	0.00	22.50	0.20	31.20	4.30	39.40	2.40
30	3P	0.00	24.60	0.20	29.80	4.00	39.20	2.20

TMB-trimethylbenzene
MB –methylbenzene
X –other product

The alkylation process is associated with a dehydratation of the ethanol (endotermic reaction) so we appreciate from our experimental results (figs. 2-4), that the optimum temperature is about 400^{0}C.

In the figure 8 is presented the chemical composition of the alkylation product for the bioethanol 100 and 96% at 400 and 450^{0}C.There is an important difference in chemical composition of the final product is more economically to carry out the process at 400^{0}C.

In the table 3 is presented the influence of the pressure on the alkylation product composition. The etylbenzene concentration is practically constant, while the diethylbenzene content in the final product, increases with the increase of the pressure.

On this experimental basis , we consider that the optimum pressure of the alkylation process is 2bar.

Conclusions

The new modified zeolitic catalyst (with Ni and Ce) has a good activity in the alkylation process of the benzene with bioethanol.

The optimum experimental conditions of the process are ratio benzene/ethanol=2/1 (mole/mole); temperature about 400^{0}C and pressure 2 bar.

Ethylbenzene is the most important component in the reaction mixture.

Using this modified catalyst, the diluted ethanol (96%) gives a better selectivity in ethylbenzene than pure ethanol.

References

1.JUN JUN YUAN,BÖRGE S .GEVERT , Indian journal of Chemical Technology **13**, july 2006 july 2006 , p 334-340.
2. SONI H.S SAMUEL V,RAMASWAMY A.V, Indian journal of Chemical, **33A** , 1994, p 844.
3. Jun Jun Yuan,Börge S .Gevert, Indian journal of chemical Technology, **11**, may 2004, p 337-345.
4.PRIMACK, H.S KATSHALL R.L, Aromatic alkylation process and apparatus, United State Patent 5087784, 02 nov 1992.
5.DWYERF.G. LEWIS P.J,SCHNEIDER F.M Chem. Eng , **83** , no 1 , 1976 p 50.
6.KEOWN P.E MEYERS C.C, WETHEROLD R.G , VS Patent, no3,1973, p 751,504.
7.GANTI , R BHATIA , S , Stud Surf Sci Catal., **54,** 1995, p171.
8.UNNIBRISNAN S, BLAT Y.S , HALGERI A.B,Indian J.Technology , **31**,1994, p 624.
9.SRIDEVI , U BHASKAR RAOB.K PRADHAN N C , Chem Eng , I , **83(3)**.(2001), p 185
10.CORMA AV , LLOPIS F, J MARTINEZ C. VALENCIA S, Journal of Catalys,**268**.2009, p 9 **.**
11.BHAT Y. S DAS J, HALGERI , AB , J Catal **155**(1995), p 154
12.DANDEKAR A. B, DEGNONT.F., M.WILLIIAMS J.P, VARKAT C.R , US Patent ,**2**,003,125,592, 2003
13. LEVESQUE P, DAO L .H, Apll Catal,**53**(1989), p 157.
14.QUDEJANS J.C VAN DE OCSTARCAMP P.F BEKKUM V.H , Appl.Catal **3** (1982), p 109.
15. NEAGU (PETRE), M., CURSARU, D., Rev Chim. (Bucharest), **64**, no 1, 2013, p.92.
16. PROSCANU, R., GANEA, R., MATEI, V., CURSARU, D., Rev Chim. (Bucharest),**64**, no 2, 2013, p. 202

Manuscript received: 25.03.2013