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Hydrocarbons from Bioethanol Conversion as Ecological Refrigerant

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Abstract

This paper aim is to present the characteristics and utilization of the products resulted from bioethanol conversion. The hydrocarbons resulted as reaction products on zeolites catalysts are similar to classical GPL and the gaseous mixture (aliphatic low hydrocarbons) were studied in order to establish their behavior as refrigerant agents in small and medium air-conditioning split systems.

Key words: *bioethanol, zeolite, C_3-C_4-iC_4, refrigerant agent, air-conditioning split system*

Introduction

Development and modernization of industrial activity, along with population growth, creates a byproduct: the phenomenon of environmental pollution which, in the context of globalization, becoming one of the most important problems of modern society, generating a negative climate and biosphere impoverishment [1, 2]. In this regard, concerns have been channeled to obtain new products and chemical and biochemical technologies development, low energy consumption and clean [1, 3, 4]. Human activities over the past century, due to "explosion" of global industrialization have led to increased greenhouse effect: uncontrolled burning of fossil fuels and deforestation have led to increased amounts of carbon dioxide discharged into the atmosphere, intensive plantations, loss of oil or gas pipelines transport, natural gas from the fermentation of household waste and manure have led to increased emissions of methane, CFC use in refrigeration has contributed to increased emissions of Freon [1]. A requirement of economic integration in the European Union is to increase capacity to produce new products or upgraded technologies and services, according to European and international standards. The success of the modernization process is conditioned by two key issues: increasing the capacity of economic agents to adjust the magnitude and rapidity of change in the economy, especially in traditional technology areas such as chemistry, restructuring and technological development [5].

It is known the capability to convert lower alcohols to ethers and hydrocarbons on zeolite catalysts. The literature data shows that temperatures, space velocity, pressure, surface condition of the catalyst and feedstock composition are the main factors influencing the reaction of lower alcohols in hydrocarbon processing. The main advantage of the catalysts of the ZSM series consists in obtaining a desired range of products and relatively low coke formation on catalysts [6, 7 and 8].

Experimental

Obtaining C_3-C_4-iC_4 fraction in bioethanol conversion

Fraction C_3-C_4-iC_4 could be used as ecological refrigerant in cooling technique as such or after separation of the components. The product comes in the form of liquefied gas under pressure [9, 10, 11]. The proposed technology uses as raw material ethanol from fermentation (bioethanol) with a minimum 78 % wt ethanol. For bioethanol conversion to C_3-C_4-iC_4 fraction it has been used a zeolite catalyst ZSM-5 type promoted with Zn.

- zeolite ZnHZSM-5: 62 %;
- matrix Al_2O_3: 33 %;
- extruded with 2.5 mm diameter and 3-6 mm length;
- specific area: 140 – 240 m^2/g;
- bulk density: 0,5 g/cm^3.

Improvement of the physical properties and catalytic performance was achieved by double promoting catalyst with Zn.

Advantages:

- increasing the stability of crystalline structure;

- reduce sensitivity to water poisoning;

- flexibility in the conversion process depending on raw material;

- controlled catalytic activity obtained by double promoting with Zn.

Catalyst deactivation during the reaction is one of the most important parameters for an industrial process from both economically and technically point of view.

For catalysts based on ZSM zeolites reversible inactivation occurs due to coke deposition and permanent deactivation due to zeolite aging as a result of long-term exposure to the action of water vapor at high temperatures. Operating parameters: temperature varied between 360 ºC and 420 ºC, and space velocity between 0.5 h^{-1} and 2 h^{-1} [6-8].

Reaction products have 44 % wt water, the reminder being hydrocarbons (gas and C_{5+}) and conversion is over 99%. Gaseous fraction consists of saturated and unsaturated C1 - C4 hydrocarbons and aqueous liquid fraction contains water and unreacted ethanol (less than 1%). Organic liquid fraction contains non-aromatic hydrocarbons (C_5-C_7) and aromatic hydrocarbons. Aromatics are benzene, toluene, xylene, C_9 and C_{10+} (duren content is below 4%, meeting the international requirements).

The three fractions resulting from the process of bioethanol catalytic conversion are separate into components. From non-condensable gas fraction are obtained ethylene-propylene fraction, ethane-propane fraction, C_4 fraction and fuel gas (ethylene-propylene fraction is used as petrochemical feedstock and fuel gas consisting mainly of hydrogen and methane can be used in hydrogenation reactions. C_3-C_4-iC_4 fraction contains a large percentage of saturated hydrocarbons, mainly isobutane, and they are compressed, cooled, subjected to liquefaction and separation of the components for use in cooling technique (the mixture can be processed with C_4 fraction from catalytic cracking or used as domestic gas. C_{5+} liquid hydrocarbon fraction can be used directly as a component for gasoline or separated in a catalytic reforming type process.

Aqueous liquid fraction is distilled to recover unreacted ethanol. Gaseous and liquid fraction composition was determined by gas-chromatography.

Presentation of air conditioning split system prototype operating with C_3-C_4-iC_4 fraction LPG type

For experimental investigations with C_3-C_4-iC_4 fraction was made an experimental bench, prototype for air conditioner split system, which made it possible to confirm the theoretical research results and conducting experimental research for performance and endurance.

Stand of a split type air conditioning was installed inside a thermostatic room in the Laboratory of Artificial Refrigeration (CCT UPB). Conditioning system for cooling that operated with C_3-C_4-iC_4 fraction comprises a refrigerating unit (compressor and forced air cooled condenser using an electrical fan) mounted inside the enclosure and a unit (evaporator with forced air cooling using an electrical fan), mounted inside the enclosure. The circuit between the two units is made using a thermally insulated copper pipe. To ensure that adjustment and the thermostatic conditioning space, the system is equipped with a remote control, respectively, with a thermostat on the air flow entering the evaporator unit. To determine the compatibility of using ecological refrigerants C_3-C_4-iC_4 type and to determine the advantages and disadvantages that arise with their use, experimental measurements of performance and endurance were made on the prototype stand.

Study of the influence of C_3-C_4-iC_4 fraction used as refrigerant on lubricating oil

To study the influence of C_3-C_4-iC_4 fraction using as refrigerant on the lubricant oil and refrigerating components, were performed analysis in order to determine the composition and physical characteristics for both the fresh lubricating oil and used lubricating oil.

To study their composition, the fresh lubricating oil and waste lubricating oil were heated in water bath in temperature range 25 °C - 100 ºC. During heating, released gases were collected in special ampoules. Collected gaseous products were then analyzed on a gas chromatograph.

Gaseous sample from both experiments (fresh lubricating oil and used lubricating oil) was introduced into the gas chromatograph by a six-way valve. The analysis was performed on a gas chromatograph Carlo Erba Instruments, Mega Series 5300, on a column filled having inner diameter di = 4mm and length L = 13 m. (20% weight) Stationary phase is β β' dipropionitril Chromosorb WAWN supported, 80-120 mesh. Mobile phase is helium. Analysis was performed at room temperature (25 °). The detector used is a thermal conductivity detector.

Results

The amount of gas in reaction products is 32 – 41 % wt, consisting in methane, ethylene, propane, propylene, butane, butenes and small amounts of C_5 hydrocarbons.

- Chemical composition: C_1 – C_5 hydrocarbons;
- Olefin content: 20 % - 56 % wt;
- Paraffin content: 32 % - 62 % wt;
- Density: 1.9 – 2.2 g/l

Organic liquid phase represents 16 – 25 % wt of global reaction products and contains C_5 - C_{12} hydrocarbons.

- Chemical composition: $C_5 – C_{12}$ hydrocarbons;
- Aromatic hydrocarbons content: 54 – 78 % wt;
- duren + izoduren: 2 – 3 % wt (maximum admitted for gasoline: 4 %);
- Density: 0.86 g/cm^3.

In reaction products, aqueous liquid phase is around 40 % wt.

- Di-ethyl-ether: traces
- Ethanol unreacted: max. 1 % wt

Ethanol conversion is over 99 %.

Table 1. Conposition of gaseous fraction

Nr. crt.	Component	amount % wt
1.	C_1	0.24
2.	C_2	8.36
3.	C_3	24.30
4.	C'_3	9.56
5.	n-C_4	8.53
6.	i-C_4	43.95
7.	1-Butena	0.38
8.	i-Butena	4.10
9.	Cis-Butena	0.58

Table 2. Organic liquid fraction

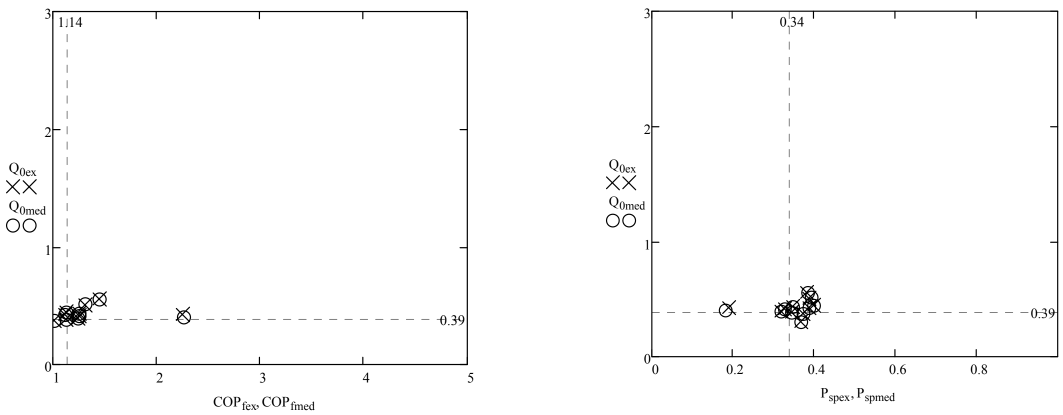
Nr. crt.	Component	amount % wt
1.	$C_5 – C_7$	40.86
2.	Benzen	2.31
3.	Toluen	12.23
4.	Etilbenzen	6.29
5.	P - Xilen	6.14
6.	M -Xilen	11.64
7.	O – Xilen	3.81
8.	Mezitilen	2.84
9.	Pseudocumen	8.04
10.	Hemimeliten	0.26
11.	Duren	2.40
12.	Prehniten	1.55
13.	C_{10+}	1.63

Table 3. Composition of aqueous liquid fraction

Nr. crt.	Component	amount % wt
1.	Water	95.50
2.	Ethanol	0.50

Following experiments carried out on the air conditioning system split type operating with (C_3-C_4-iC_4 fraction LPG type, the following average values of system performance were obtained, as is summarized in the two charts in figure 1 (a, b): cooling power (Q_0)= 390 W; electric power needed for cooling compressor (P_{sp}) = 340 W, coefficient of performance of the refrigeration energy (COP) = 1,14.

Comparing the experimental performance values when split was loaded with C_3-C_4-iC_4 fraction, having the concentration shown in table 1, with those obtained when it was used as refrigerant C_3-C_4-iC_4 fraction LPG type, it result that the best performances were obtained when using C_3-C_4-iC_4 fraction LPG type. Thus, this justifies to approval C_3-C_4-iC_4 fraction LPG type as refrigerant for small and medium air conditioning systems.



a) b)

Fig.1. Average values of performance of air-conditioning system split type operating on C_3-C_4-iC_4 LPG type fraction.
a) C_3-C_4-iC_4; b) C_3-C_4-iC_4, LPG type

To study the influence of using C_3-C_4-iC_4 fraction as refrigerant on lubricant oil and refrigeration installations components, physical properties of the fresh and used lubricant oil were determined, as well as the composition of fresh lubricant oil and used lubricant oil. Physical properties are presented in table 4.

Table 4. Physical properties of the fresh and used lubricant oil

Physical property	Fresh lubricant oil	Waste lubricant oil
Density d4/20	0.8704	0.8732
Refraction index, n D/20	1.4829	1.4687
Sulphur, % wt	0.95	0.31
Ignition temperature, °C	154	52-53
Viscosity, 40 °C, cSt	34.27	26.71
Viscosity, 70 °C, cSt	24.69	12.6
Viscosity, 100 °C, cSt	18.3	6.84

Comparing data for fresh and waste lubricants, it can be seen that for the lubricant used in refrigeration with C_3-C_4-iC_4 as refrigerant, the ignition temperature values are decreasing (from 154 ºC for fresh lubricant to 52-53 ºC for waste lubricant), as well as viscosity values.

For the waste lubricant oil the variation of viscosity with temperature shows a more pronounced decrease at higher temperatures (70 ºC and 100 ºC) compared with fresh lubricant oil. This may be due to changes in oil composition by increasing the share of lighter products, so the C_3-C_4-

iC_4. The variation of viscosity with temperature for fresh lubricant and waste lubricant at 40 ºC, 70 ºC and 100 ºC it is represented in figure 2.

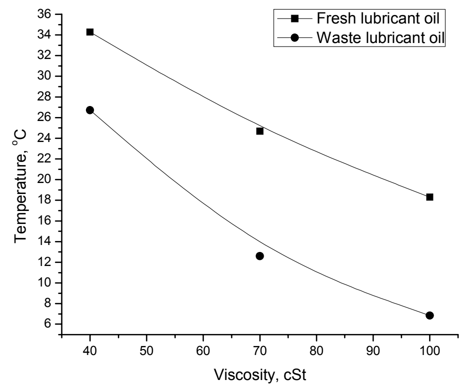


Fig. 2. Variation of viscosity with temperature for fresh lubricant and waste lubricant at 40 ºC, 70 ºC and 100 ºC

For 100 ml fresh lubricant oil less than 50 cm^3 gaseous products were collected and for 100 ml of waste lubricant oil more than 100 cm^3 gaseous products were collected, and that confirms the above formulated hypothesis concerning the viscosity decreasing due to the lubricant oil enrichment in light fraction.

Composition for gaseous product resulted from fresh lubricant oil heating was, according to GC report in figure 4 (for gas % mol = % vol): 79,8 % ethane and 20,2 % iso-butane (retention times were determined using reference materials: 14,42 s for ethane, respectively 24,17 s for iso-butane)

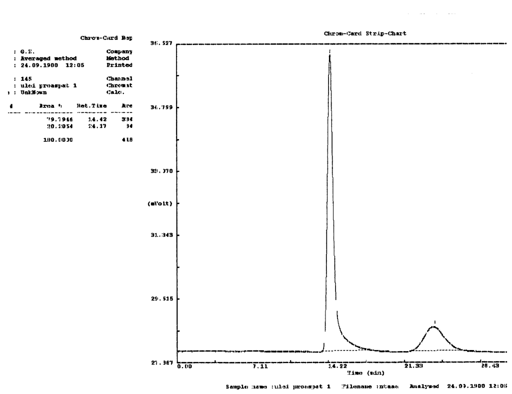


Fig. 3. Composition of gaseous reaction product from fresh lubricant oil heating

Composition of gaseous reaction product from the heating of the waste lubricant oil was, according to GC report in figure 4 (for gas % mol = % vol): 40,71 % ethane, 0,56 % ethylene, 13,08 % propane, 16,3 % propylene, 7,36 % butene 1, 0,56 % iso-butene, 11,56 % trans 2 butene and 9,67 % cis 2 butene (retention times were determined using reference materials).

It could be seen that it wasn't obtained saturated C_4 fraction, meaning butane and isobutene, in the gaseous product resulted from waste lubricant oil heating.

It is noted that the waste lubricant oil has been used for six months in refrigeration systems with C_3-C_4-iC_4 fraction as refrigerant.

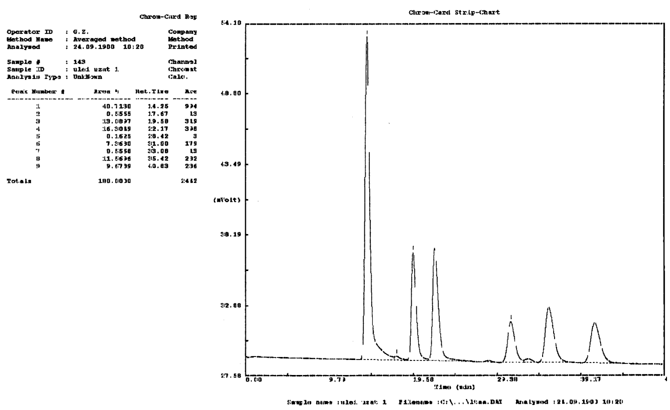


Fig. 4. Composition of gaseous reaction product from waste lubricant oil heating

Conclusions

There were analyzed mixtures of C_3-C_4-iC_4 having different concentrations. The results obtained show that air-conditioning system has the best performances when is utilized C_3-C_4-iC_4 LPG type fraction. Depending on season, the composition of LPG is C_3 35 % wt in winter and 15 % wt in summer. Experimental study show that air-conditioning system performances not differ more than 5 % - for season different concentrations - from industrial LPG.

According to ASHRAE refrigerants classification, butane and propane are considered to be A3 type (non-toxic and flammable), also specific to C_3-C_4-iC_4 LPG type fraction.

Performance experiments on the stand were held on two stages: 1707 hours, respectively 2183 hours. The average performances of air-conditioning system using as refrigerant C_3-C_4-iC_4 LPG type fraction, were: evaporator cooling power– 920 W, electric power needed for cooling compressor – 360 W, coefficient of performance of the refrigeration energy – 2.56. These values allow to place the air-conditioning split system that use C_3-C_4-iC_4 LPG type fraction in energy class „E”.

During experiments (3890 ore) there were not technical failures. This confirms the good compatibility of C_3-C_4-iC_4 LPG type fraction with the materials and lubricant of conditioning system. If all the values of performance indicatives are stationary it results a good reliability of the product.

Because the C_3-C_4-iC_4 LPG type fraction is a mixture of substances A3 type, it is reccomended its use as refrigerant in air-conditioning systems with small and medium cooling power such is the split type.

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Hidrocarburi din bioetanol – agenti frigorific ecologici

Rezumat

Acest articol prezinta caracterizarea si utilizarea produselor rezultate din conversia bioetanolului. Hidrocarburile rezultate din conversia bioetanolului pe catalizatori zeolitici sunt asemanatoare cu cele din compozitia GPL-ului si acest amestec gazos (hidrocarburi alifatice inferioare) a fost studiat pentru a stabili comportramentul ca si agenti frigorifici in instalatii mici si medii de aer conditionat de tip split.