



**HETEROGENEOUS CATALYTIC OLIGOMERIZATION  
OF OLEFIN-CONTAINING FRACTIONS OF HYDROCARBONS  
PYROLYSIS LIQUID PRODUCTS AS A REASONABLE WAY  
OF THEIR UTILIZATION**

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**ABSTRACT**

The work is devoted to the obtaining of co-oligomers from the byproducts of ethylene production. The above products were obtained using heterogeneous acidic catalysts having the nature of silica-alumina. The specific surface area of the catalysts was defined by methylene blue adsorption method. The yields and properties of the products obtained in the presence of various catalysts were analyzed. The relationship between the structure of the catalyst and its effectiveness in the co-oligomerization process was analyzed.

Keywords: liquid pyrolysis products, catalytic oligomerization, heterogeneous catalysts, silica-alumina materials, methylene blue adsorption method

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**INTRODUCTION**

The main source of raw materials, so important for organic synthesis as ethylene, propylene and butylenes, is the pyrolysis of hydrocarbons such as gasoline, diesel fuel, etc. However, along with the target gaseous products, liquid products (byproducts) of pyrolysis are also formed. Their yields vary in the range 20-40% depending on the feedstock and the process conditions [1]. The C<sub>5</sub> and C<sub>9</sub> fractions are the prevailing part of these products. The above fractions are complex mixtures of saturated and unsaturated hydrocarbons of the aliphatic

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(C<sub>5</sub>) and aromatic or cycloaliphatic series. Utilization of these petrochemical byproducts is a real problem of great economic and ecological importance. The most reasonable way to utilize the fractions of liquid pyrolysis products is their oligomerization to obtain co-oligomers (petroleum resins) which have a wide range of applications. The products are used in paints and varnishes, in the rubber industry, papermaking, printing inks, corrosion-resistant coatings, pavements, for woodworking and fiberboard production, for various building materials and composite materials production, etc. [2].

The products may be obtained by thermal, initiated and catalytic co-oligomerization. Thermal oligomerization requires high temperatures and pressures, and the final product yields are relatively low. The initiated oligomerization also enables low product yields. It is characterized by long duration. Additionally, peroxide initiators are highly explosive and fire-hazardous. Most usually, co-oligomeric products from olefin fractions are obtained by homogeneous catalytic co-oligomerization with Friedel-Crafts or Ziegler-Natta catalysts. The existing technologies have a number of significant disadvantages. First of all, besides the oligomerization itself, they include stages of catalyst decomposition with the solution of alkali and washing off of the salts formed. This results in approximately 6 Mg (megagram) of hazardous contaminated wastewater being discharged to the environment for each ton of product obtained [1]. As a result, the catalyst itself is irreversibly lost. When exposed to moisture, the formation of highly corrosive media occurs, which requires additional costs for protecting the equipment from corrosion and for drying the feed. These catalysts are unstable on storage and quickly lose their activity. Besides, the co-oligomers obtained using this method have low unsaturation and are often too dark. Our research aimed at developing an efficient technology to produce co-oligomeric products from waste generated by the petrochemical industry, without the aforementioned disadvantages. In addition, the technology should be environmentally safe and not expensive.

The use of heterogeneous catalysts of oxide nature, which have acidic properties, enables avoiding the neutralization and washing stages as the catalyst can easily be separated by filtering. As a result, the problem of waste water is solved and the number of process stages is reduced. These catalysts are very cheap, they do not lose their activity on storage and do not create corrosion aggressive media.

One of the key indicators of the heterogeneous catalyst effectiveness is the value of its specific surface area. Therefore, the problem was to find a relationship between the obtained co-oligomeric product yields and values of the specific surface area of the catalysts in the presence of which these products were obtained.

In heterogeneous catalysis, the method of N<sub>2</sub> adsorption (or He and Ar mixture adsorption), which is based on the Brunauer-Emmet-Teller (BET) equation, is most commonly used for determination of the specific surface area of the catalysts. However, the method requires much time as well as precise and expensive equipment. Under the circumstances, a cheap and simple method is desirable which, on the other hand, provides accurate and relevant results. The

BET method is not very suitable for such an important class of catalysts and adsorbents, as the swelling of clay minerals occurs. This is due to the peculiarities of the clay structure, namely the layered sandwich structure of their structural elements [3]. The  $N_2$  adsorption method provides the value of only the outer surface of such materials because nitrogen molecules cannot penetrate into the clay interlayer space (in the dry state separate layers are closely adjacent to each other) [4, 5]. When getting wet, these clays swell, interlayer spacing increases and the entire surface becomes available.

The “wet” method of the specific surface area determination (in contrast to the “dry”, or BET, method) enables the aforementioned problems to be solved. The method is based on the titration of water suspensions of the studied catalyst with a methylene blue solution.

Methylene blue (or 3,7-bis(dimethylamino)phenothiazin-5-ium chloride according to the IUPAC nomenclature) is a cationic dye that is able to be adsorbed on the surface of silica-alumina materials by interaction with acidic sites of the surface [5]:

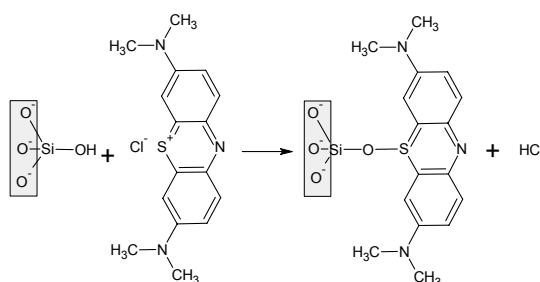


Fig. 1. Methylene blue adsorption.

Methylene blue molecules have a flat, rectangular shape and their dimensions are  $17\text{\AA} \times 7.6\text{\AA} \times 3.25\text{\AA}$  [5]. During adsorption onto the surface methylene, the blue molecule is placed in such a way that its largest side is almost parallel to the surface:

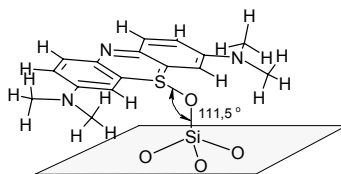


Fig. 2. Adsorbed methylene blue molecule arrangement relative to the surface.

The area covered with an adsorbed methylene blue molecule is about  $130\text{\AA}^2$  [5]. Thus, knowing how much of methylene blue the weighed amount of the catalyst is able to adsorb, we can roughly calculate the specific surface area of the catalyst.

Because of a sufficiently large size of monomer molecules: styrene ( $\approx 7.5\text{\AA}\times 4.5\text{\AA}$ ) and dicyclopentadiene ( $\approx 6,5\text{\AA}\times 5\text{\AA}$ ), they often cannot penetrate into the catalyst active sites located on its inner surface, especially in the case of microporous catalysts. Thus, even for a very large specific surface area, the catalyst may be ineffective because much of the surface remains inaccessible to the reagents and does not participate in the process. Therefore, it is important to determine not only the total specific surface area, but also how much of the surface is accessible to the reagents.

Methylene blue adsorption method is the optimal solution in this case. Large molecules of methylene blue are not able to penetrate into the micropores of catalysts and to be adsorbed on their inner surface. Since methylene blue molecules are larger than the molecules of the C<sub>9</sub> fraction components, it can confidently be stated that pores and cracks, which the methylene blue molecules can penetrate into, will be accessible to the reagent molecules in the co-oligomerization process. Thus, the specific surface area determined by this method, actually, is the active (accessible) surface area to be determined.

## EXPERIMENTAL PART

### The object of research

The object of our study was the heterogeneous-catalytic co-oligomerization of the C<sub>9</sub> fraction of liquid pyrolysis products of diesel fuel. The approximate composition of the above-mentioned fraction was determined by gas-liquid chromatography (Table 1). The main unsaturated substances that the C<sub>9</sub> fraction consists of are styrene and dicyclopentadiene and, to a much lesser extent, vinyltoluenes. Accordingly, the co-oligomeric products obtained from such a feed consist mainly of styrene and dicyclopentadiene links.

Table 1. Ingredients of the C<sub>9</sub> fraction of diesel fuel pyrolysis liquid products.

Name of substance	Content, % by wt.	Name of substance	Content, % by wt.
Styrene	18.93	Xylenes	16.84
Dicyclopentadiene	17.78	Ethyltoluenes	7.02
Vinyltoluenes	8.13	Pseudocumene	6.73
$\alpha$ -Methylstyrene	1.97	Mesitylene	2.18
Indene	1.93	Hemimelitol	1.84
Allylbenzene	0.86	Ethylbenzene	1.65
Other unsaturated ones	8.02	n-Propylbenzene	0.80
Total (unsaturated)	57.62	Indane	0.56
		Cumene	0.41
		Other saturated ones	4.35
		Total (saturated)	42.38

## Catalysts

A number of silica-alumina materials, namely zeolites (NaX, NaY, CaA and natural clinoptilolite), clays (bentonite, kaolin, palygorskite, monotermitite), as well as silica and alumina, were investigated as catalysts of the C<sub>9</sub> fraction co-oligomerization

Silica-alumina materials were activated before use. Activation of catalysts consists in treatment with a 13% by wt. solution of sulfuric acid at 100°C for 6 hours [6, 7]. As a result of the activation, the content of SiO<sub>2</sub> increases, while the amount of Na<sub>2</sub>O, CaO, MgO and Al<sub>2</sub>O<sub>3</sub> is reduced [6-8]. Due to chemical treatment, the acidity of aluminosilicate increases, since both zeolites and clays are capable of ion exchange and alkali metal ions are replaced by protons [3, 7-9]. In addition, the formation of additional pores occurs, the pore diameter, total porosity and specific surface area increase [6-8] because of partial dissolution of such network-forming ions as Al<sup>3+</sup>, Mg<sup>2+</sup>, Fe<sup>3+</sup>.

### Obtaining the co-oligomers from the C<sub>9</sub> fraction of diesel fuel pyrolysis liquid products

Oligomerization of the C<sub>9</sub> fraction of liquid pyrolysis products was carried out at a temperature of 80°C for 3 hours under argon with continuous, intense stirring. The amount of the catalyst in the reaction mixture was 15% by wt in all cases. Before use, the catalyst was dried at 100-150°C for one hour. After co-oligomerization the catalyst was filtered out under vacuum. Atmospheric and vacuum stripping were carried out to obtain the final product in the residue.

### The properties of the obtained products

Such parameters as the softening point (by the ring-and-ball method), average molar weight (by the cryoscopic method using Beckman thermometer), color (iodine scale), unsaturation (bromine number) and density (using the Westphal-Mohr balance) were defined for the obtained co-oligomers. The density of the co-oligomerizate before stripping was also determined with an aerometer.

### Determination of the catalysts' specific surface area

Determination of specific surface area was carried out as follows. The methylene blue solution was prepared by mixing 1 g of methylene blue dry powder with 200 ml of deionized water. Three grams of an oven-dried catalyst was mixed with 10 ml of deionized water. The suspension was stirred intensely with a magnetic stirrer during titration. The methylene blue solution was added into the suspension with 0.5 ml increments. After each addition, the suspension was mixed for 1 minute. Then a small drop was removed from the suspension with a glass rod and placed onto filter paper. If the unabsorbed methylene blue is present in the solution it forms a permanent blue halo around the suspension

aggregate spot [5]. This means that methylene blue has covered all the surface of the test sample (end-point).

Based on the quantity ( $V_{MB}^{titr.}$ , ml) of the methylene blue solution needed for a total coverage of the catalyst surface (end-point), the catalyst's specific surface area ( $SSA$ ,  $m^2/g$ ) may be determined.

$$SSA = \frac{V_{MB}^{titr.} \cdot N_A \cdot S_{MB} \cdot m_{MB}}{M_{MB} \cdot V_{MB}}$$

wherein

- $M_{MB}$  – methylene blue molar weight ( $M_{MB} = 319.87$  g/mol),
- $N_A$  – Avogadro's number ( $N_A = 6.023 \cdot 10^{23}$  mol<sup>-1</sup>),
- $S_{MB}$  – the area covered with one methylene blue molecule ( $S_{MB} = 130 \text{ \AA}^2$ ),
- $m_{MB}$  – mass of methylene blue used for the solution preparation,
- $V_{MB}$  – volume of the prepared methylene blue solution,
- $V_{MB}^{titr.}$  – methylene blue solution volume used for the titration.

## RESULTS AND DISCUSSION

The main criterion of the catalyst efficiency is the co-oligomeric product yield. In the presence of the investigated catalysts, the following co-oligomer yields were obtained.

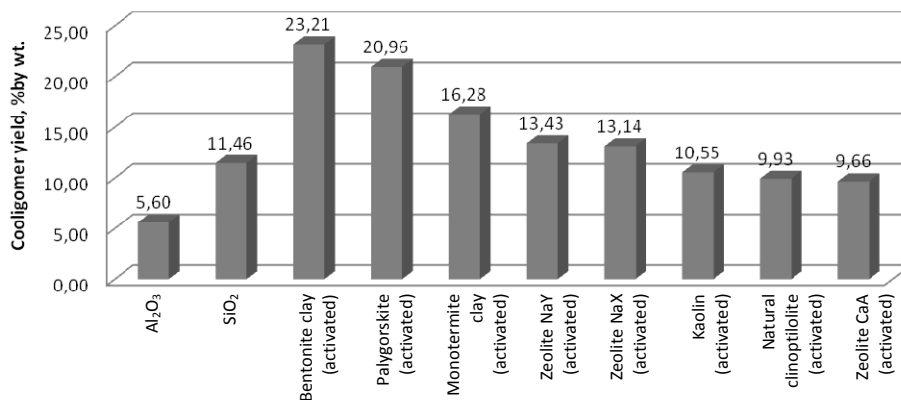


Fig. 3. Product yields obtained in the presence of different catalysts.

The above chart shows that the highest yields were achieved in the presence of natural clay materials such as bentonite, palygorskite and, to a lesser extent, monotermite.

Determination of the specific surface area of the investigated catalysts provided the following results presented in Fig. 4.

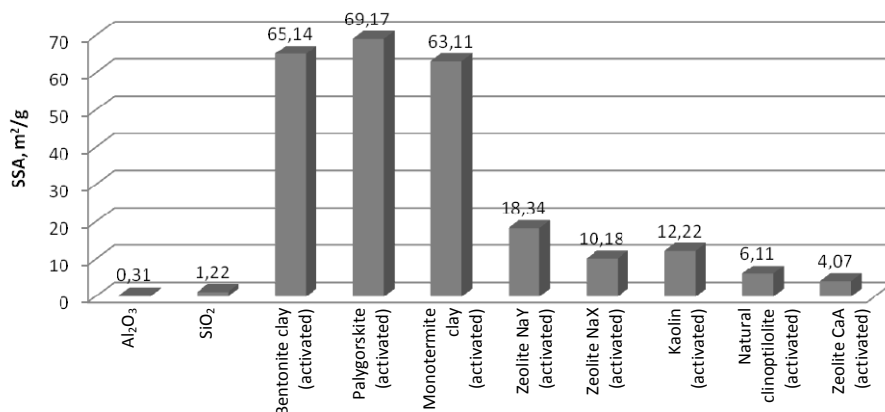


Fig. 4. The catalysts' specific surface area, determined by methylene blue adsorption method.

It is clear from the chart that the three catalysts, which enabled the highest yields to be achieved, have the largest specific surface area. These are: activated bentonite clay, palygorskite, and monotermite clay. Another clay studied, kaolin, which belongs to non-swelling clays, has a considerably smaller specific surface area. In the case of the investigated zeolites, the total specific surface area, which is up to 1000 m<sup>2</sup>/g according to literature [9], only 1-2% of this area is accessible to the reagents' molecules. The specific surface area is larger for the large pore zeolites NaX and NaY than for the microporous ones, like CaA or natural clinoptilolite. All of this affects the yields of the product obtained in the presence of these catalysts. The "KCM1" brand silica used by the present authors also belongs to microporous materials, which is why less than 0.5% of its total specific surface area, that is, about 500 m<sup>2</sup>/g [6], participates in the co-oligomerization process. Thus we can conclude that spongy-type aluminosilicates including zeolites are much less effective in the process in comparison with corpuscular-type aluminosilicates. In particular bentonite clay has a lamellar layered structure, and palygorskite has a matted fibrous and needle structure. The separate microparticles in such materials are not interconnected, unlike zeolites, which have a fixed, rigid crystalline structure.

The obtained products are solid glassy transparent materials of which the colors range from peach to dark red. Other properties of the products obtained when using various catalysts are shown in Table 2.

The average molar weight is lower for those catalysts which enable higher yields to be achieved. Thus, an inverse relationship between the values of yield and molar weight is observed.

Probably the same reason determines the high yield, and leads to lower values of the product's molar weight. The greater the number of the catalyst active sites participating in the process, the greater the number of chains simultaneously initiating and, consequently, a lower molar weight product is ob-

tained. The parameter can easily be adjusted by reducing the amount of catalyst in the reaction mixture. This reduces the yield but increases the co-oligomer's molar weight. Experiments carried out with 1, 5, 10 and 15% catalyst concentration confirmed the above statement.

Table 2. The properties of the co-oligomeric products obtained by heterogeneous catalytic co-oligomerization of diesel fuel pyrolysis liquid products.

Catalyst	M, g/mol	SP, °C	Br number mg Br <sub>2</sub> /100 g	Color, mg I <sub>2</sub> /100 ml	ρ(PR), kg/m <sup>3</sup>
Al <sub>2</sub> O <sub>3</sub>	780.2	92	48.0	120	1062.0
SiO <sub>2</sub>	563.7	70	61.9	260	1070.7
Bentonite clay (activated)	597.3	58	69.9	130	1070.1
Palygorskite (activated)	684.1	85	72.5	140	1073.3
Monotermite clay (activated)	558.8	81	71.9	130	1070.9
Zeolite NaY (activated)	665.5	65	69.4	130	1067.9
Zeolite NaX (activated)	758.9	90	70.1	150	1069.0
Kaolin (activated)	866.5	100	61.1	250	1043.4
Natural clinoptilolite (activated)	1581.8	109	53.0	160	1060.8
Zeolite CaA (activated)	1264.8	102	57.8	120	1057.5

The values of the softening point (SP) of the obtained resins generally correlate with the product's molar weights and prove a similar dependence.

As far as the density (ρ(PR)) of the obtained co-oligomers is concerned, we can say that it is the higher, the lower is the product's average molar weight. As a matter of fact, its value varies in a narrow range (1043.4 – 1073.3 kg/m<sup>3</sup>). This result can be explained as follows. The lower the co-oligomer macromolecule, the closer they can be packed, and hence the density of the product is higher. However, this dependence is not quantitative and perhaps there is the effect of other factors.

High unsaturation of the products is especially worth noting. If resins produced in a homogeneous catalytic process have a bromine number of about 20-35 mgBr<sub>2</sub>/100 g, in the case of the investigated silica-alumina catalysts the co-oligomer's bromine number was about 53-72 mgBr<sub>2</sub>/100 g. When analyzing high unsaturation of products, attention ought to be paid to the C<sub>9</sub> fraction composition (Table 1).

Dicyclopentadiene (DCPD) deserves special attention as a monomer. Since dicyclopentadiene (tricyclo[5.2.1.0<sup>2,6</sup>]deca-3,8-diene) has a strained ring, and two double bonds: norbornene and cyclopentene ones, the mechanism of its oligomerization may consist in individual polymerization reactions and/or ring opening [11]. In addition, whether the dominant product formation reaction proceeds according to one or other mechanism is largely determined by the catalytic system used. Therefore, when oligomerization by a norbornene double



bond, which is much more reactive than that of cyclopentene, takes place the reaction proceeds as follows:

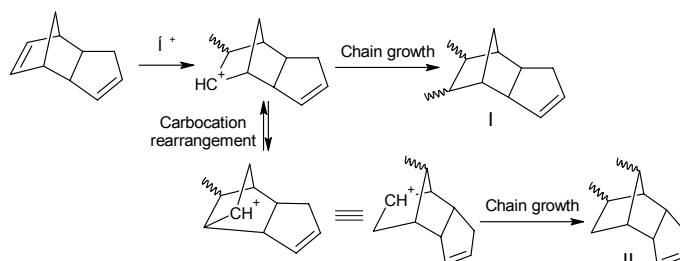


Fig. 5. Scheme of DCPD oligomerization by norbornene double bond.

Structures I and II, containing residual double bond in each link, are mainly formed in this case. While oligomerization by cyclopentene double bond takes place, structure III is predominately formed, though the formation of structure IV is also possible.

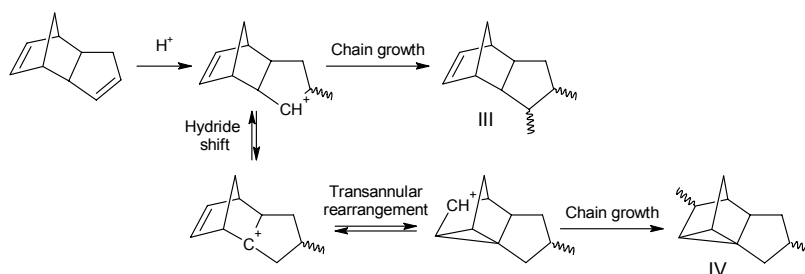


Fig. 6. Scheme of DCPD oligomerization by cyclopentene double bond.

In addition to the above mentioned mechanisms of oligomerization, which consist in polymerisation by a norbornene or cyclopentene double bond, there is another mechanism of oligomerization, namely the ring opening metathesis oligomerization [12]:

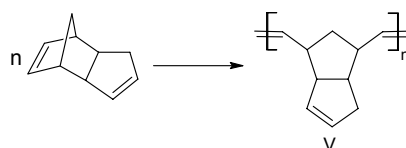


Fig. 7. Ring opening metathesis oligomerization of dicyclopentadiene.

At the ring opening metathesis oligomerization the number of double bonds is not reduced and, consequently, the most unsaturated oligomeric product is obtained. This mechanism is desired the most. High bromine numbers suggest that dicyclopentadiene oligomerization proceeds to a considerable

extent by metathesis mechanism with norbornene ring opening (Fig. 7). It is reasonable to use Raman spectroscopy to verify this supposition [13].

## CONCLUSIONS

A number of silica-alumina materials were investigated as the C<sub>9</sub> fraction of a diesel fuel pyrolysis liquid products oligomerization catalyst. Analysis of the results authorizes a conclusion that natural silica-alumina materials, activated with acid, can serve as an oligomerization catalyst. Natural clay minerals such as bentonite and palygorskite after acid activation proved to be particularly effective catalysts for the process. It was shown how the basic properties of the product vary when different catalysts are used. It was found that the use of a silica-alumina catalyst enables highly unsaturated co-oligomers to be obtained. High unsaturation makes them especially good film-forming agents, as well as valuable components of composite materials and rubbers.

The results of the specific surface area measurements indicate that there is a relation between the values of available specific surface area of catalysts and the yields of co-oligomeric products obtained in the presence of these catalysts. It was experimentally confirmed that clay materials, such as bentonite clay, have high specific surface areas which is accessible to the reagents. The relations between specific surface area and yield are not quantitative probably because of different acid surface active sites concentration for different catalysts. Taking that into account, we can assume that the number of active acid sites in activated zeolites is much higher than in the studied activated clays. Investigation of the number and strength of active surface sites of these catalysts is one of the further tasks of our research.

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