Multiple Use of Silica-Alumina Catalyst in Hydrocarbon Resins Production

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Abstract – Hydrocarbon resins synthesis from C_9 fraction of liquid products of diesel fuel pyrolysis when using activated bentonite clay as a catalyst at multiple use of the latter has been studied. Process is analysed in terms of the resin yield and its properties including average molecular weight, colour and bromine number. The results obtained are explained considering the catalyst characteristics. The process when using the used catalyst undergone to high temperature regeneration has also been carried out. The catalyst regeneration has been studied by thermogravimetric analysis. Reasonable application areas of the used catalyst are suggested.

Key words – hydrocarbon resins, C_9 fraction, cooligomerization, heterogeneous catalyst, activated bentonite clay, multiple use of a catalyst, catalyst regeneration.

I. Introduction

Synthesis of hydrocarbon resins is one of the most reasonable ways of utilization of liquid pyrolysis by-products, being formed in lower olefins productions. Hydrocarbon resins are low-molecular cooligomers having wide application. They are used in paints and varnishes, tackifiers, hot melt, pressure sensitive and solvent adhesives, sealants, rubber compounding, papermaking, printing inks, corrosion-resistant coating, pavement and road marking, for woodworking and fibreboard production, for various building materials and composite materials production [1-11].

C_9 fraction of hydrocarbon feed pyrolysis liquid products is an object of our research. The fraction contains about 50 wt. % of polymerizable hydrocarbons, dominant of which are styrene, dicyclopentadiene and viniltoluenes. Hydrocarbon resins from C_9 fraction are produced either by radical (thermal or initiated) or cationic (when using Friedel-Krafts or Ziegler-Natta catalysts) cooligomerization [1, 2]. We have suggested to use heterogeneous silica-alumina catalysts to synthesize the hydrocarbon resins from the C_9 fraction. Having studied the number of silica-alumina catalysts we have chosen the optimal one – activated bentonite clay [12-14]. Considerable reserves of bentonite clays in Ukraine (e.g. Dashukivka deposit of 104.7 million tonnes) and their low price (about 0.2$/kg) make it economically feasible to use such catalyst.

One of the key advantages of heterogeneous catalysis over homogeneous is possibility of a catalyst multiple use. That is why it was necessary to investigate the multiple use of the activated bentonite clay (ABC) in hydrocarbon resins synthesis process. It is the problem the present paper is dedicated to.

II. Hydrocarbon resin yield at multiple use of the catalyst

To ascertain the possibility of the ABC multiple use as C_9 fraction monomers cooligomerization catalyst, the synthesis has been carried out with the ABC that had been already used in the process (hereinafter ABCU for short).

ABC was used five times in succession. The process was carried out under conditions specified in Fig. 1. As can be seen in Fig. 1, the yield decreases by about a third at the second use of the catalyst.
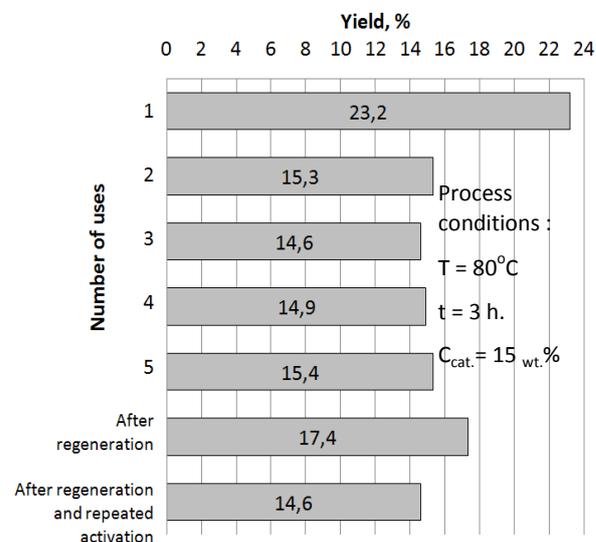
Fig. 1. Hydrocarbon resin yield at multiple use of the catalyst

So, it is hardly correct to say that ABC is reusable catalyst in the hydrocarbon resins synthesis process. However, the subsequent uses of the catalyst result in almost the same yield as in case of the second use.

Colour of ABCU is different from that of ABC. Fresh catalyst has light-beige colour. After usage it becomes gray. This, obviously, denotes the presence of residual cooligomers on the catalyst surface.

SEM of ABC and ABCU shows that the catalyst surface changes after being used (Fig. 2).
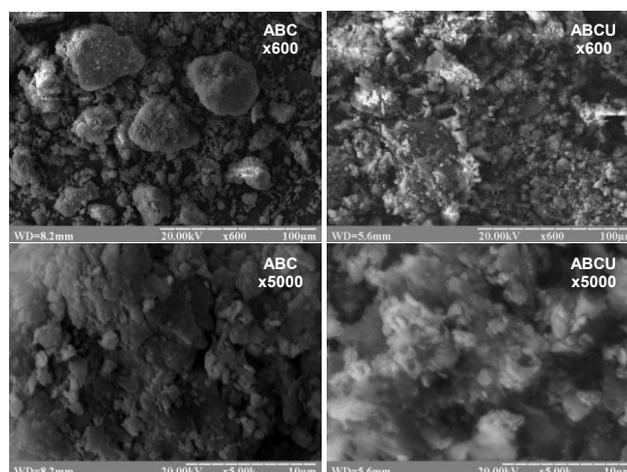
Fig. 2. SEM images of fresh catalyst (left) and the catalyst having been used in cooligomerization (right)

Even at small magnification (Fig. 2, top) it is clear that the surface structure of ABCU (Fig. 2. right) differs from that of fresh ABC (Fig. 2, left). At high magnification it can be seen that separate particles and element of the surface have fuzzy edges and becomes somewhat truncated. This confirms that there are cooligomer molecules on the catalyst surface.

In case of ABC, cooligomerization proceeds on the surface active sites. The sites generally are surface hydroxyl groups [15-17]. The oligomerization can be schematically represented as follows (Fig. 3).
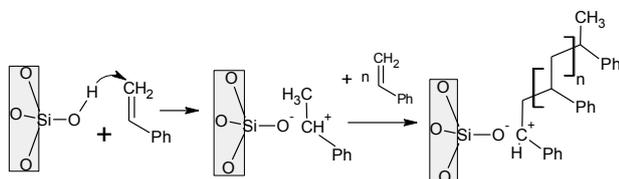
Fig. 3. Heterogeneous catalytic oligomerization scheme (in terms of styrene)

The cooligomer detachment from the catalyst occurs as shown in Fig. 4 (1 and 2). But some of the macromolecules do not detach and remain at the catalyst surface. The ion pair may also be transformed to the covalent bond (Fig. 4 (3)).
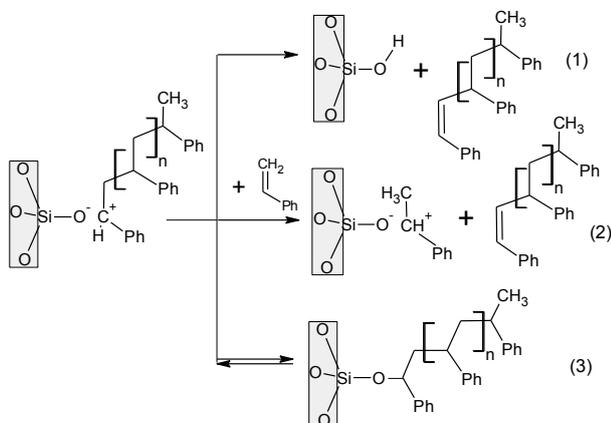
Fig. 4. Chain termination schemes in case of heterogeneous catalytic cooligomerization (in terms of styrene)

In consideration of the fact that the product yield decreases by a third at second use of the catalyst but remains almost constant at further uses (Fig. 1) it may be assumed that some fraction of active sites is irreversibly deactivated with cooligomers, while the rest of the sites are not.

TABLE 1

ACTIVE SITES CONCENTRATION, STRENGTH AND DISTRIBUTION

Active site type	pK_a	H_S, mmol/g	Fraction, %
1	4.63	0.165	33
2	10.10	0.140	28
3	5.87	0.125	25
4	7.86	0.070	14
Average / Total	6.39	0.501	-

The catalyst has been studied in terms of the active sites concentration, their strength (pKa) and distribution of the sites of different strength. Potentiometric titration followed by computer data treatment using specialized software ProtoFit [17-20] was used for this aim.

It has been ascertained that there are four types of the active sites in the activated bentonite clay (Table 1).

Propagating cooligomeric chain being macrocarbocation per se is bound with negatively charged counterion by electrostatic force. In case of stronger active site the electron density is pulled off the oxygen atom more strongly and the partial negative charge on it is reduced. As a result the electrostatic force holding the macrocarbocation is also reduced. So, the cooligomeric chain propagating on active surface site is detached (Fig. 4 (1 and 2)) the easier the stronger the active site is. Considering the above said, it can be assumed that the sites with pK=10.10 (and, probably, with pK=7.86 as well) are deactivated after the first use of the catalyst and don't participate in cooligomerization any more that causes the yield decrease.

III. Hydrocarbon resin properties at multiple use of the catalyst

Application areas of the hydrocarbon resins from the C_9 fraction are determined by the resins properties, firstly by colour, unsaturation (bromine number (BN)) and average molecular weight. So, it was an important task to find out how do the cooligomers key properties change at multiple use of the catalyst (Table 2).

TABLE 2

PROPERTIES OF HYDROCARBON RESINS AT THE CATALYST MULTIPLE USE

Number of uses	Average molecular weight	BN, g Br_2 / 100 g	Colour, mg I_2 / 100 ml
1	600	69.9	130
2	680	68.9	400
3	740	67.6	600
4	740	68.3	600
5	660	68.7	600
After regeneration	600	73.5	130
After regeneration and repeated activation	610	71.4	130

The cooligomer obtained with fresh ABC has fairly light colour – 130 mg I_2/100 ml (by standard iodine scale). In case of the catalyst reuse, however, the colour considerably deteriorates and remains equal to 600 mg I_2/100 ml for the 3rd, 4th and 5th uses. Hydrocarbon resins of such dark colour are inapplicable in paint and varnishes of light colours and paper production. However, colour does not matter when the resin is used in rubbers, road pavements, composite and building materials, paints and varnishes of dark colours etc.

Average molecular weight of the resin obtained when using fresh ABC is 600 indicating the 5-6 monomer units to constitute the cooligomer. In case of the catalyst reuse the average molecular weight increases by 110 units on the average. The cooligomer molecular weight increases, most probably, due to the decrease of number of catalytic active acid sites participating in cooligomerization. As has been determined earlier [13], molecular weight decreases when the number of active acid sites increases. In case of catalyst reuse the active sites number decrease has an adverse effect: less number of cooligomer chains is initiated simultaneously. As a result cooligomers of higher molecular weight (660-740) may be formed.

In case of fresh ABC the resin BN is 69.9 g Br_2/100 g. In case of the catalyst reuse the product unsaturation decreases very inessentially and BN remains high (67.6 – 68.9 g Br_2/100 g).

Comparison of FT-IR spectra of the cooligomers synthesized when using ABC and ABCU, other conditions being equal, (Fig. 5) shows that most spectra regions are identical.
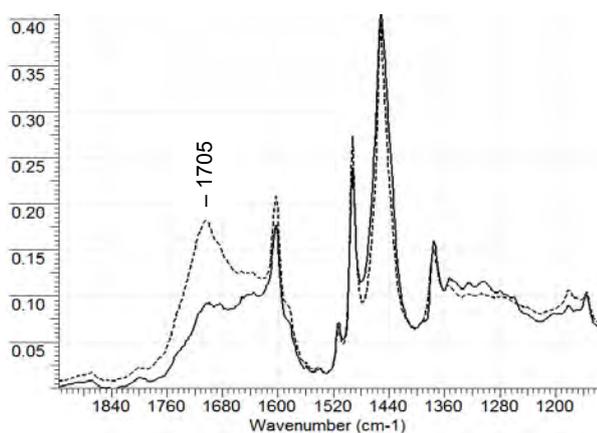
Fig. 5. FT-IR spectra of the cooligomers obtained at first (——) and second (·········) use of the catalyst

The main difference is the presence of the intensive absorption at 1705 sm^{-1} in the spectrum of the product obtained with ABCU. There is no such peak in the spectrum of the cooligomer obtained with ABC (Fig. 5). This peak corresponds to stretching vibrations of C=O bonds of carboxyl groups. It denotes the product obtained with ABCU to be more oxidized.

The carboxyl groups, most probably, are formed as a result of the methylene groups of cyclopentene rings of the DCPD units oxidation. These groups are very reactive and under the influence of light and atmospheric oxygen changes to a fulvene-like structure (Fig. 6) [2].
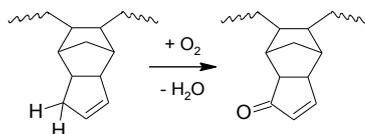
Fig. 6. DCPD units oxidation resulting in cooligomer intensive colouration

Chromophore structures are characteristic of fulvenes. That is why all such structures are intensely yellow,

orange, or brown in colour. So, the presence of even small quantities of this type of structure may have a considerable effect on the cooligomer colour. It explains why the cooligomer obtained with used catalyst has such dark colour.

Broad absorption area at 3200-3600 sm^{-1} is a bit more intensive in the spectrum of the cooligomer synthesized at the catalyst reuse that also indicates this product to be more oxidized.

IV. Catalyst regeneration

Since the catalyst activity decrease is caused by the blockage of part of active sites by cooligomer molecules, the removing of these molecules by the catalyst regeneration should restore the catalyst activity and increase the yield. The regeneration of ABCU was carried out in the muffle furnace at 400°C for 4 h. As a result the organic substances adsorbed on the catalyst surface were burned out under the influence of atmospheric oxygen. After the regeneration the catalyst colour became light-beige again just as that of the fresh ABC.

Average particle size of the catalyst after the regeneration is 426 nm, while particle size of fresh ABC is 420 nm, i.e. it is almost the same.

The regenerated catalyst has been used in cooligomerization of polymerizable components of C_9 fraction. The yield obtained was 17.4 wt. % (Fig. 1). It is more than in case of ABCU (~15 wt. %), but much less than in case of fresh ABC (23.2 wt. %).

The process of the used catalyst regeneration has been studied by thermogravimetric analysis (TGA) (heating rate was 10°C/min.). As is clear from Fig. 6, the weight loss begins already at 50°C, but occurs very slowly. Intensive burning of organic matter begins at 270°C and reaches maximum rate at 373°C (smaller peak of the differential curve). That is why there is no reason to carry out the regeneration at temperature higher than 400°C. Further dramatic loss of weight is obviously caused by superposition of the effects of organic matter burning and the catalyst surface dehydration.
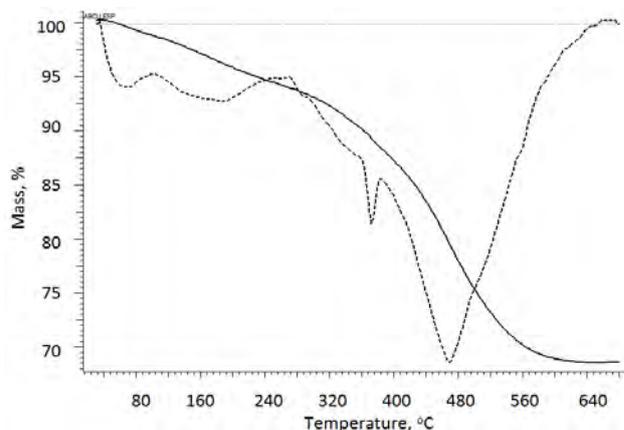
Fig. 7. TGA curve for ABCU (·········· – dm/dT)

TGA results for ABCU have to be compared with TGA results for ABC. As we can see from Fig. 8, temperature increase from the beginning results in weight loss that is

caused by desorption of water absorbed on the catalyst surface. Maximum rate of this process occurs at 75°C. The peak at the same temperature in the TGA curve of ABCU (Fig. 7) denotes the same process to occur – absorbed water desorption. It should be noted that the weight loss due to water desorption is much greater in case of the fresh catalyst (Fig. 8) compared to that in case of used one (Fig. 7). This indicates relatively high hydrophobicity of ABCU surface.
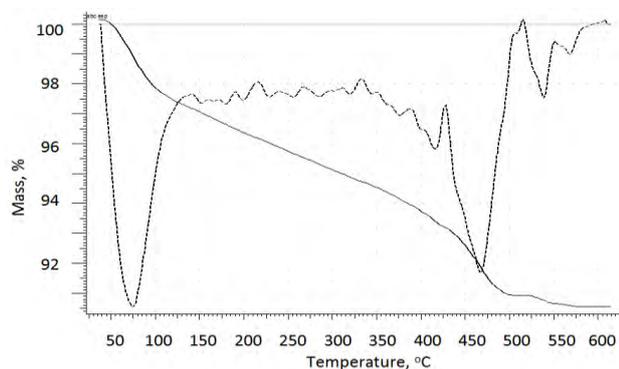
Fig. 8. TGA curve for ABC (............ – dm/dT)

The surface dehydration for fresh ABC begins at about 400°C and reacts maximum rate at 468°C (Fig. 8). Location of the main peak of TGA curve of ABCU in the same place (Fig. 7) indicates the same process to occur during ABCU regeneration.

Total weight loss of ABC due to dehydration is about 5 wt. % (Fig. 8). The reason why the catalyst initial activity is not restored is, obviously, the surface partial dehydration. The surface acid Brønsted sites (surface hydroxyl groups), on which the oligomerization proceeds [15-17], are irreversibly converted into siloxane groups as a result of dehydration (Fig. 9).
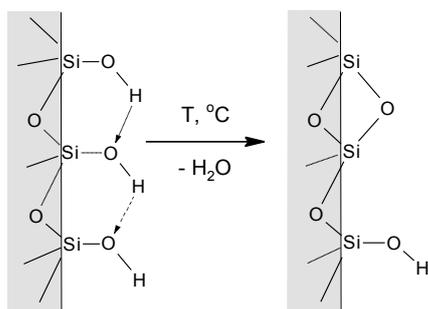
Fig. 9. Catalyst surface thermal dehydration scheme.

TGA results of the regenerated catalyst (Fig. 10) definitely proved the above conclusion. When comparing TGA curves for the fresh and regenerated catalyst, it is clear that the weight loss due to the surface dehydration is very slight (1.1 wt. %) in case of the regenerated catalyst. So, there is very small amount of surface hydroxyl groups retained after the regeneration to be dehydrated.

Elemental composition of ABC before and after being used, as well as after the regeneration (ABCR), has been determined by energy-dispersive X-ray spectroscopy (Table 3).
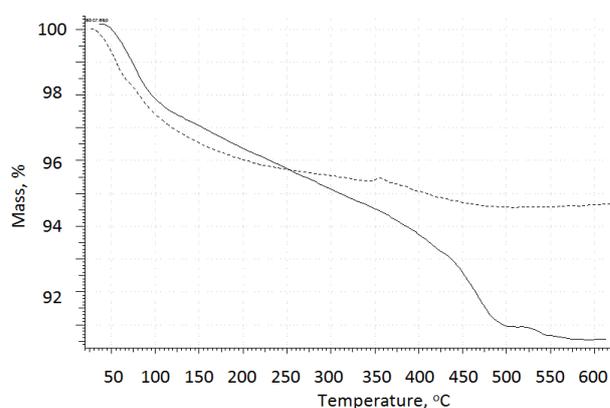
Fig. 10. Comparison of TGA curves for fresh (——) and regenerated (..........) catalyst

TABLE 3

Elemental composition of the catalyst

Chemical element	Element percentage in		
	ABC	ABCU	ABCR
C	0.0	7.6	0.0
O	32.1	26.0	29.4
Na	0.6	0.5	0.6
Mg	0.7	0.7	0.7
Al	12.8	12.2	12.8
Si	51.4	50.8	54.3
S	0.6	0.6	0.4
K	0.3	0.3	0.3
Ca	0.1	0.0	0.0
Ti	0.4	0.3	0.4
Fe	1.1	1.0	1.2

Results given in Table 3, indicates considerable amount of carbon in ABCU. Elemental composition of the regenerated catalyst is almost the same as that of fresh ABC. The only essential difference is decrease of oxygen content in the regenerated catalyst by 2.7 wt. % compared to fresh one. It also proves the catalyst surface dehydration.

Maximum rate of absorbed cooligomers burning is achieved at 373°C, while the surface dehydration leading to the catalyst deactivation begins to proceed intensively at about 400°C. So, it could be expected that the catalyst can be regenerated without being deactivated when carrying the regeneration out at temperatures below 400°C. However, the temperature on the catalyst surface considerably exceeds the set temperature of the furnace due to the thermal effect of burning. Thus, the catalyst surface dehydration is inevitable during the regeneration.

Total weight loss of ABCU is 31 wt. % (Fig. 7), 5.5 wt.% of which are caused by water desorption. The rest 25.6 wt. % of the loss are caused by cooligomers burning out and the surface dehydration. Taking into account that the weight loss due to the surface dehydration is about 5 wt. % (Fig. 8), it can be stated that the cooligomer content in the used catalyst is about 20.6 wt. % of the ABCU total weight. Thus, if the catalyst content in the reaction mixture is 15 wt. %, the loss of the cooligomer with ABCU is 3.6 wt. % of the feedstock, i.e. 15.6 wt.% of the total amount of the cooligomer formed. It is clear that this number would be less at lower concentration of the

catalyst and under conditions enabling to achieve higher yield.

Repeated activation of the regenerated catalyst gives no positive effect. The resin yield achieved with regenerated and repeatedly activated catalyst is even less than in case of ABCU use (Fig. 1).

The resins obtained with regenerated catalyst have the same light colour as those synthesized with fresh ABC – 130 mg I_2/100 ml. Repeated activation of the regenerated catalyst has no impact on the product colour and it is 130 mg I_2/100 ml as well (Table 2).

Use of the regenerated catalyst allows obtaining the cooligomer with BN equal to 73.5 g Br_2/100 g, that is no less than BN of the product obtained with the fresh catalyst (69.9 g Br_2/100 g) (Table 2).

V. Used catalyst applications

If the ABC is not used multiply, the problem of ABCU utilization arises. It is especially important as the heterogeneous catalyst is used in relatively great amount.

Since the used catalyst is of silica-alumina nature, it can be used in building materials production. In particular, it is known that montmorillonite and hydromica clays are the best raw materials for haydite production [21]. Bentonite clay belongs to such clays [17]. The organic admixtures present in ABCU would be absent in the haydite, because all organic substances would be readily burned out under the haydite production temperature (up to 1200°C in air medium). Moreover, some organic admixtures are sometimes added to the clay raw material to enhance the haydite blowout [21]. So, the presence of organic substances in ABCU may have a positive impact on the quality of the haydite produced from such raw material.

It is also known that various aluminosilicates, and first and foremost clays, are used as fillers of bitumen, facilitating rheological properties of the latter. In particular, bentonite clay and attapulgite are suggested to be used as bitumen ultrafillers [22]. Montmorillonite and bentonite clay are also considered to be mechanical stabilizers of bitumen [23]. Not pure bentonite clay but one modified with organic substances are often used to be introduced into bitumen [24]. It has been shown that bentonite clay modified (aminated) with octadecylammonium chloride affects the properties of bitumen much better than unmodified clay. The modification makes clay hydrophobic and more consistent with bitumen [24].

Inorganic lubricants, main of which are silica, graphite and bentonite lubricants, are an important class of industrial lubricants [25]. Bentonite lubricants consist of a dispersing medium (mostly hydrocarbon oils) and a thickener. Bentonite clay hydrophobized by means of amination is used as a thickener in bentonite lubricants. Ammonium salts with long hydrocarbon chains (e.g. octadecylammonium acetate, dimethyldialkylammonium chlorides, benzyldimethylalkylammonium chlorides etc.) are used for this aim. Such lubricants have good hydrolytic stability and may be used in friction units exploited at temperatures up to 150°C [25].

Our used catalyst is hydrophobized by cooligomeric chains bound to its surface. As we have ascertained, they are not wetted with water. Thus, there is no need to carry out clay modification using expensive organic modifiers, and ABCU may be used both for bitumen modification and for industrial lubricants production.

Conclusions

The repeated use of the heterogeneous catalyst (activated bentonite clay) in C_9 fraction monomers cooligomerization allows to achieve the resin yield by a third less than in case of the fresh catalyst use. It is caused by the weak active sites (sites with high pKa) deactivation by the cooligomer residues.

However, in the subsequent uses of the catalyst the cooligomer yield is almost constant.

When the catalyst concentration is $C_{cat.}$ = 15 wt. % and the process temperature T = 80°C the loss of the cooligomer with the used catalyst is 15.6 wt. % of the total amount of the cooligomer formed.

The cooligomers obtained with ABCU have much darker colour and somewhat higher molecular weight compared to the product synthesized with fresh ABC.

High temperature regeneration of the used catalyst increases the resin yield a little bit, but does not restore the catalyst activity in full. It is because irreversible process of the catalyst surface dehydration during the regeneration.

Taking into account the low price of ABC and high cost of energy carriers, it is, probably, more reasonable to use every time the fresh catalyst than regenerated one.

Anyway, depending on the hydrocarbon resins application, manufacturer can decide how it is more reasonable to produce them: if the light colour of the resins is required, it is necessary to use fresh or regenerated catalyst, if it is not required, multiple use of the activated bentonite clay may be acceptable. Production of light and dark resins in amounts and ratio determined by the demand is also possible.

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