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РАЗРАБОТКА ТЕХНОЛОГИИ ПОЛУЧЕНИЯ НЕФТЕПОЛИМЕРНЫХ СМОЛ ИЗ ФРАКЦИИ C_9 С ДОЗИРОВАНИЕМ КАТАЛИЗАТОРА И ЦИКЛОПЕНТАДИЕНА

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В работе представлены результаты исследования процессов получения углеводородных смол на основе светлых продуктов пиролиза нафты (прямогонного бензина) с пределами выкипания 130-210 °С. Каталитическая полимеризация данных фракций является перспективным промышленным направлением ввиду более полного использования мономеров при условии решения проблем дезактивакции катализаторов. Эти проблемы частично решаются при использовании гомогенных катализаторов и применении методов синтеза, не предусматривающих использование катализатора или удаление продуктов дезактивации катализатора из полимера. Были рассмотрены результаты полимеризации вышеупомянутой фракции жидких продуктов пиролиза в присутствии каталитической системы на основе тетрахлорида титана и эквимолярного количества диэтилалюминий хлорида, а также дополнительного активного мономера – циклопентадиена, при температуре 20 °С. В работе были использованы способы дозирования как катализатора, так и активного мономера. Показано, что постепенное дозированное добавление реагентов дает возможность проводить процесс при более низких температурах по сравнению с инициированными или термическими процессами полимеризации, стабилизировать скорость реакции на первой стадии и достичь более высокой конверсии смолообразующих компонентов. ^{1}Н ЯМР-спектры смол указывают на фрагментарное подобие получаемых смол полимерам на основе фракции C_5 - C_9. Полученные смолы обладают высокими температурами размягчения и непредельностью. Сочетание этого варианта с полной дезактивацией компонентов каталитического комплекса при технической реализации выглядит предпочтительнее высокотемпературных технологий. Данная разработка может быть реализована при создании промышленных технологий получения нефтеполимерных смол на основе стандартного емкостного оборудования, а также при разработке непрерывной схемы производства.

Ключевые слова: нефтяные смолы, жидкие продукты пиролиза, дициклопентадиеновые фракции, циклопентадиен

DEVELOPMENT OF PETROLEUM RESINS TECHNOLOGY PRODUCING FROM THE C_9 FRACTION WITH DOSING OF A CATALYST AND CYCLOPENTADIENE

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The paper presents the results of studying the processes of obtaining hydrocarbon resins based on light naphtha (straight-run gasoline) pyrolysis products with boiling temperature of 130-210 °C. Catalytic polymerization of these fractions is a promising industrial direction due to more complete use of monomers, provided that the problems of catalyst deactivation are solved. These problems are partially solved by using homogeneous catalysts and applying deactivation methods that do not involve removing the catalyst deactivation products from the polymer. The results of polymerization of the above-mentioned fraction of liquid pyrolysis products in the presence of a catalytic system based on titanium tetrachloride and an equimolar amount of diethylaluminum chloride, as well as an additional active monomer - cyclopentadiene, at a temperature of 20 °C were considered. The work used dosing methods for both the catalyst and the active monomer. It is shown that gradual dosed addition of reagents makes it possible to carry out the process at lower temperatures compared to initiated or thermal polymerization processes, stabilize the reaction rate at the first stage and achieve higher conversion of resin-forming components. ^{1}H NMR-spectra of resins indicate fragmentary similarity of the obtained resins to polymers based on the C_5 - C_9 fraction. The obtained resins have high softening temperatures and unsaturation. The combination of this option with complete deactivation of the components of the catalytic complex during technical implementation seems preferable to high-temperature technologies. This development can be implemented in the creation of industrial technologies for the production of petroleum polymer resins based on standard tank equipment, as well as in the development of a continuous production scheme.

Keywords: petroleum resins, liquid pyrolysis products, dicyclopentadiene fractions, cyclopentadiene

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INTRODUCTION

Petroleum resins (PR) have traditionally been the object of research due to their demand in various industries: the paintwork materials industry as film-forming agents [1], sealants [2], adhesive components [3], the rubber and tire industries as softeners and compatibilizers [4], in the road industry to improve the properties of binders [5], for the production of cryogels in demand in the conditions of the Far North [6]. The nomenclature of petroleum resins is extensive and is primarily determined by the choice of fractions included in liquid pyrolysis products [7] with boiling points ranging from 40 to 210 °C. In general, the initial temperature of the fractions of liquid pyrolysis products used to produce the so-called light PR is determined by the boiling point of the C_5 fraction, while the final temperature is determined by the choice of the consumer or the decision of the manufacturer, with a typical range of 180-210 °C. There are technical possibilities to combine or divide fractions of liquid pyrolysis products depending on market requirements, which leads to a significant expansion of the range of petroleum resins. Finally, various initiators [8], catalysts [9], catalytic systems [10, 11]), thermal initiation [12] can be used to produce resins. Resins can be modified with derivatives of unsaturated carboxylic acids [13], halogens [14], hydrogenation [15, 16], oxidative methods [17, 18], nitration [19] and can be used as other resins in polymer composites [20].

The choice between initiated and catalytic methods for obtaining polymerization products is dependent on the composition and structure of the mono-

mers included in the fraction. In general, the use of catalytic polymerization methods is indicated when a significant number of diene monomers are present, whereas the choice of radical initiation of the process, including thermal and initiated polymerization methods, is mainly applicable to monoolefins, particularly those of the styrene series, which most fully represent the fractions C_8 - C_{10}, C_9.

The presence of diene and styrene type comonomers in the fraction in close concentrations, which are difficult to separate either technically or for economic reasons, leads to solutions that implement the resin production process in several stages.

The authors of the article [21] showed on the basis of plant data that by changing the operating parameters of the depentanizer within acceptable limits, it is possible to obtain working fractions with different ratios of reactive monomers, during the polymerization of which hydrocarbon resins of various types can be obtained. It was also established [22] that dicyclopentadiene fractions after complete or partial distillation become extremely active, as a result of which the yield of petroleum polymer resin increases. This occurs as a result of the decomposition of dicyclopentadiene (DCPD) with the formation of cyclopentadiene (CPD). This reaction is reversible and over time, reactive cyclopentadiene is converted into a dimeric product.

Thus, it seems logical to develop technical solutions at the stage of depentanization of pyrolysis products, or to implement options for partial recycling of DCPD and CPD, which are used to compound high-boiling fractions. The first option does not require capital investments for installing additional equipment, but changing the operating mode of the columns partially affects the component composition of the material flows. The second option for separating DCPD and CPD from fractions C_5 and C_9 does not affect the operation of the depentanizer, but requires the creation of a DCPD decomposition section.

The implementation of the process of modifying the compositions of light fractions is a probable and acceptable, but the requirements of reproducibility of physico-chemical and technical characteristics require the organization of control over the composition of raw materials due to its constant change due to the course of the CPD dimerization reaction.

The method of introducing the catalyst has a significant effect on the synthesis of PR [23]. Polymerization of the styrene fraction (150-200 °C) at 60 °C with a single introduction of the $AlCl_3$–acetone–butanol–water complex leads to a resin yield of 26.7%. Fractional introduction of the catalytic system leads to a more complete conversion of the monomers, with a resin yield of 69.6% based on the initial raw material, with a T of about 100 °C and a color of mg I_2 / 100 ml.

In the presented work, the process of copolymerization of the C_9 fraction with cyclopentadiene under the action of $TiCl_4$ and the $TiCl_4$ - $Al(C_2H_5)_2Cl$ catalytic system has been considered and the influence of several methods of introducing CPD and a catalyst on the yield and characteristics of resins has been evaluated.

EXPERIMENTAL PART

The C_9 fraction with an unsaturated hydrocarbon content of 52% was used as a feedstock (JSC Angarsk Polymer Plant). Dicyclopentadiene with 99,0% purity (Akros Company). Titanium tetrachloride with 99,6% purity (Ecotech Plant). Nitrogen, purity 99,996% vol. Diethylaluminium chloride, 20% solution in heptane (Tomskneftekhim LLC).

Cyclopentadiene (comonomer) with a base substance content of 94-97% was obtained by DCPD distillation in a nitrogen atmosphere and added to the C_9 fraction. The total amount of CPD used was 12%.

The process was carried out in a glass reactor in a nitrogen atmosphere at 20 °C. A single catalyst loading was carried out at 10 °C and then the temperature was maintained at 20 °C for 180 min. Titanium tetrachloride was deactivated by adding propylene oxide at a molar ratio of 1:4. The resin yield was determined by sampling after distilling off volatile components at a temperature of 150 °C for 0.5 h at 10 mBar.

Polymerization with $TiCl_4$ – $Al(C_2H_5)_2Cl$ system was carried out using a method similar to the one described above for polymerization under the action of $TiCl_4$.

Polymerization using $TiCl_4$

In the first series of experiments, options for the synthesis of petroleum r resins with a one-time loading of the catalyst into the C_9 fraction were considered. In this section of the work, the $TiCl_4$ catalyst was used.

Fig. 1 shows graphs of the dependence of the PR yield on time with a one-time addition of a catalyst and various methods of adding CPD.

It follows from the graphs shown in Fig. 1 that polymerization, regardless of the method of loading the catalyst and the comonomer, is mostly completed in 60 min. In the variant of the process without the addition of CPD, the yield was about 27%, which corresponds to the conversion of 52% of all unsaturated components of the fraction, including the least reactive monomers.

Carrying out processes with dosing or one-time loading of cyclopentadiene into the C_9 fraction leads to a significant increase in the polymerization

rate. The resin yield reaches 40-42% in 60 min, reaching 43-46% by the end of the process. Obviously, when considering the above options for loading reagents, the increase in the yield of petroleum resin (16-18%) is mainly determined by the amount of reactive monomer added, but exceeds the additive result.

The results of polymerization of the C_9 fraction with the dosed addition of a catalyst and CPD are shown in Fig. 2.

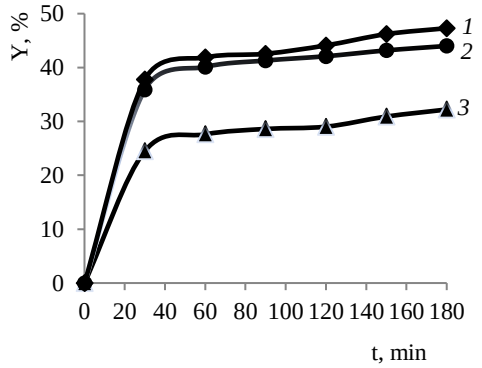

Fig. 1. Dependence of the PR yield (Y, %) on the method of synthesis, 2% $TiCl_4$, 20 °C: 1 – one-time loading of the catalyst, dosing of CPD for 120 min; 2 – one-time loading of the catalyst and CPD; 3 – one-time loading of the catalyst (without CPD)

Рис. 1. Зависимость выхода НПС от способа проведения синтеза, 2% $TiCl_4$, 20°С: 1 – одноразовая загрузка катализатора, затем дозирование ЦПД в течение 120 мин; 2 – одноразовая загрузка катализатора и ЦПД; 3 – одноразовая загрузка катализатора (без ЦПД)

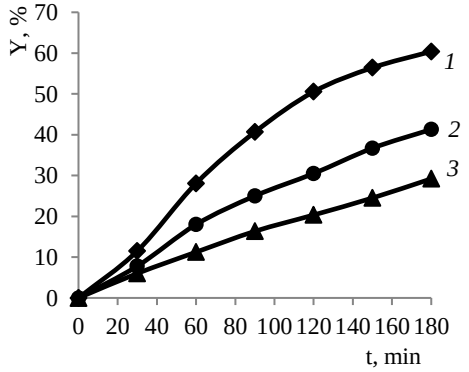

Fig. 2. Dependence of the PR yield (Y, %) on the method of synthesis, 2% $TiCl_4$, 20 °C: 1 – dosing of the CPD and catalyst into the fraction for 120 min; 2 – one-time loading of the CPD and metered loading of the catalyst for 120 min; 3 – dosing of the catalyst (without CPD) for 120 min

Рис. 2. Зависимость выхода НПС от способа проведения синтеза, 2% $TiCl_4$, 20 °С: 1 – дозированная загрузка ЦПД и катализатора во фракцию в течение 120 мин; 2 – одноразовая загрузка ЦПД и дозированная загрузка катализатора в течение 120 мин; 3 – дозированная загрузка катализатора (без ЦПД) в течение 120 мин

Dosing of the catalyst results in a higher yield of the product compared to a single loading. Without adding CPD, the process ends with a yield of PR of about 25% (Fig. 2, curve 3). Adding cyclopentadiene to the fraction leads to an increase in the resin yield by 10% (Fig. 2, curve 2), and simultaneous dosing of the catalyst and CPD leads to a polymer yield of 54%.

Thus, a single loading (Fig. 1, curve 3) and dosed loading (Fig. 2, curve 3) of equal amounts of catalyst do not have advantages over each other in terms of resin yield.

With a single full addition of cyclopentadiene, an increase in the resin yield of 10-12% is achieved, while with dosing – by 16-18%. Thus, with the portionwise addition of $TiCl_4$, the yield of PR reaches 41%, and dosing cyclopentadiene for 120 min with a total process time of 180 min leads to a yield of PR equal to 47%. Simultaneous dosing of the catalyst and cyclopentadiene to the fraction allows achieving the maximum yield of resin compared to other solutions (Fig. 2, curve 1). Obviously, the determining factor for achieving the maximum yield of petroleum polymer resin is the addition of active monomer. And although dosing increases the duration of synthesis by 1.5 times, the increased yield and quality of the product pays for the costs.

Table 1

Characteristics of the obtained PR (2% $TiCl_4$, 20 °C)

***Таблица 1.* Характеристики полученных НПС (2% $TiCl_4$, 20 °C)**

Production methods *	Yield, % mass	Color **	Molecular weight	BN **	$T_{soft.}$, °C
1	60	200	610	84	115
2	41	150	610	62	97
3	29	600	560	70	100
4	47	150	650	76	105
5	44	200	560	73	107
6	32	610	470	61	100

Примечания: *Способы получения: 1 – дозирование ЦПД и катализатора в C_9; 2 – одноразовая загрузка ЦПД в C_9, затем дозирование катализатора; 3 – дозирование катализатора в C_9 (без ЦПД); 4 – одноразовая загрузка катализатора в C_9, затем дозирование ЦПД; 5 – одновременная загрузка ЦПД и катализатора в C_9; 6 – одноразовая загрузка катализатора в C_9 (без ЦПД)

**Показатели: цвет – цвет 50 % -го раствора по йодометрической шкале, мг I_2/ 100 г KI; БЧ – бромное число, г Br_2/ 100 г НПС, $T_{разм}$, °С – температура размягчения смолы, °С

Notes: *Production methods: 1 – dosing of CPD and catalyst into C_9; 2 – one-time loading of CPD into C_9, then dosing of catalyst; 3 – dosing of catalyst into C_9 (without CPD); 4 – one-time loading of catalyst into C_9, then dosing of CPD; 5 – simultaneous loading of CPD and catalyst into C_9; 6 – one-time loading of catalyst into C_9 (without CPD);

**Indicators: color – color of 50% solution on iodometric scale, mg I_2/100 g KI; BN – bromine number, g Br_2/100 g PR; $T_{soft.}$, °C – resin softening temperature, °C

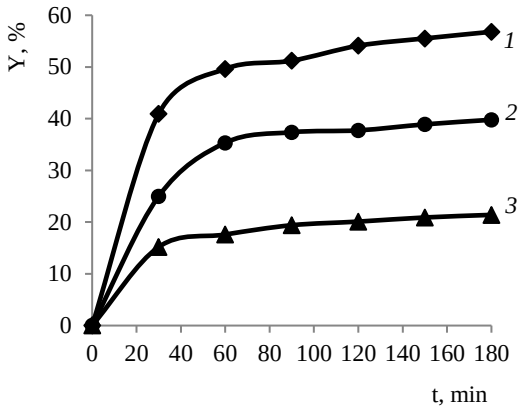

Fig. 3. Dependence of the PR yield (Y, %) on the method of synthesis, 2% $TiCl_4$ – $Al(C_2H_5)_2Cl$ (1 : 1 mol), 20 °C: 1 – one-time loading of CS, dosing of CPD for 120 min; 2 – simultaneous one-time loading of CPD and catalytic system; 3 – one-time loading of catalytic systems (without CPD)

Рис. 3. Зависимость выхода НПС от способа проведения синтеза, 2% $TiCl_4$ – $Al(C_2H_5)_2Cl$ (1 : 1 моль), 20 °C: 1 – одноразовая загрузка КС, дозирование ЦПД в течение 120 мин; 2 – одновременная одноразовая загрузка ЦПД и каталитической системы; 3 – одноразовая загрузка каталитической системы (без ЦПД)

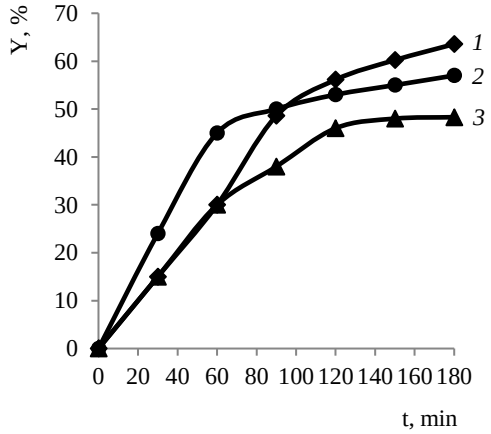

Fig. 4. Dependence of the PR yield (Y, %) on time for various synthesis methods, 2 % $TiCl_4$ – $Al(C_2H_5)_2Cl$ (1 : 1 mol), 20 °C: 1 – dosing of the CPD and the catalytic system for 120 min; 2 – one-time CPD, dosing of the catalytic system for 120 min; 3 – portion loading of the catalytic system to the C_9 fraction (without CPD)

Рис. 4. Зависимость выхода НПС от времени при различных способах проведения синтеза, 2 % $TiCl_4$ – $Al(C_2H_5)_2Cl$ (1 : 1 моль), 20 °C: 1 – дозирование ЦПД и каталитической системы в течение 120 мин; 2 – одноразовая загрузка ЦПД, дозирование каталитической системы в течение 120 мин; 3 – порционная загрузка каталитической системы к фракции С9 (без ЦПД)

It is obvious that the properties of the obtained resins (Table 1) can vary to a certain extent with changes in the process conditions: the molecular weight is in the range from 450 to 650 g/mol, the color of the product reaches 200 mg I_2 / 100 g KI. The expectations that the dosing of cyclopentadiene and catalyst leads to the formation of the most unsaturated resins were also confirmed.

Polymerization using the $TiCl_4$ – $Al(C_2H_5)_2Cl$ catalytic system

Further, polymerization of the C_9 fraction using the catalytic system (CS) $TiCl_4$ – $Al(C_2H_5)_2Cl$, taken in an equimolar ratio, was carried out using similar methods.

The dependences of resin yields on the time of synthesis for various methods of applying CPD and the catalytic system are shown in Fig. 3, 4.

The graphs shown in Figs. 1 and 3 and illustrating the processes of synthesis of PR with a one-time loading of the $TiCl_4$ catalyst and the $TiCl_4$ – $Al(C_2H_5)_2Cl$ catalytic system, respectively, are similar. Polymerization mostly ends after 60 min, then the increase in resin yield is insignificant. It should be noted that the use of a catalytic system (Fig. 3, curve 3) without the addition of a CPD leads to a noticeably lower PPR yield compared with the use of $TiCl_4$ (Fig. 1, curve 3). The option with simultaneous single loading of all reagents, including CPD, also does not give an advantage when using the $TiCl_4$ – $Al(C_2H_5)_2Cl$ catalytic system. The PR yield is also lower compared to using $TiCl_4$.

However, in the case of CPD dosing, the use of a catalytic system allows for a higher resin yield compared to the use of a $TiCl_4$ catalyst. The increase in resin yield is noticeably higher than the amount of CPD added, both in the first (Fig. 1, curve 1) and in the second (Fig. 3, curve 1) cases. It is possible to talk about the specific interaction of the CPD with the catalytic system with the formation of active intermediate monomers. From the analysis of curves 1-3 of Fig. 3, it clearly follows that an increase in the reactivity of the C_9 fraction with the addition of CPD leads to an increase in product yield by 19%, and dosing of CPD for 120 min increases the yield of PR by 37%.

When dosing the CPD and the catalyst (Fig. 4, curve 1), the resin yield increases almost linearly during 120 min, reaching a maximum value by 180 min, while with a one-time loading of the catalyst and dosing of the CPD for 120 min (Fig. 3, curve 1), the process is almost completed in 60 min.

The characteristics of petroleum polymer resins obtained using the $TiCl_4$ – $Al(C_2H_5)_2Cl$ catalytic system are presented in Table 2.

When considering the results presented in Table 2, it can be concluded that the use of CPD as a reactive comonomer makes it possible to increase the yield of PR by an amount significantly exceeding its additive. The choice of the synthesis method, which consists in the dosed administration of both the catalytic system and the CPD, allows to achieve a significantly higher yield than can be expected when calculating according to the additive scheme.

Table 2

Characteristics of the obtained PR (2% $TiCl_4$ – $Al(C_2H_5)_2Cl$ (1:1 mol), 20 °C)

***Таблица 2.* Характеристики полученных НПС (2% $TiCl_4$ – $Al(C_2H_5)_2Cl$ (1 : 1 моль), 20 °C)**

Production methods *	Yield, % mass	Color *	Molecular weight	BN **	$T_{soft.}$, °C
7	64	150	680	73	110
8	57	200	640	72	100
9	48	250	420	67	95
10	58	150	770	72	97
11	40	250	510	76	100
12	21	600	330	64	100

Примечания: *Способы получения: 7 – дозирование ЦПД и КС в С9; 8 – одноразовая загрузка ЦПД в C_9, затем дозирование КС; 9 – дозирование КС в C_9 (без ЦПД); 10 – одноразовая загрузка КС в C_9, затем дозирование ЦПД; 11 – одновременная загрузка ЦПД и КС в C_9; 12 – одновременная загрузка КС в C_9 (без ЦПД);
**Показатели: цвет – цвет 50 % -го раствора по йодометрической шкале, мг I_2/ 100 г KI; БЧ – бромное число, г Br_2/ 100 г НПС; $T_{разм}$, °С – температура размягчения смолы, °С
Notes: *Production methods: 7 – dosing of CPD and KS in C_9; 8 – one-time loading of CPD in C_9, then dosing of KS; 9 – dosing of KS in C_9 (without CPD); 10 – one-time loading of KS in C_9, then dosing of CPD; 11 – simultaneous loading of CPD and KS in C_9; 12 – simultaneous loading of KS in C_9 without CPD); **Indicators: color – color of 50% solution on iodometric scale, mg I_2/100 g KI; BN – bromine number, g Br_2/100 g PR; $T_{soft.}$, °C – resin softening temperature, °C

The resins obtained by dosing the catalytic system and CPD are significantly lighter than those without CPD. An increase in molecular weight is also observed, which is associated with increased activity of CPD in polymerization processes. Probably, this is also associated with a slight increase in the bromine number of resins when using CPD, a diene series modifier.

CONCLUSION

1. The influence of the method of carrying out the polymerization process of the C_9 fraction: the addition of a catalyst/catalytic system, cyclopentadiene as an active comonomer, on the yield and characteristics of the petroleum polymer resin have been studied. The possibility of obtaining light unsaturated oligomeric products at a temperature of 20 °C with a yield of up to 60-64% and softening point in the range 95-115 °C has been shown.

2. When using the $TiCl_4$ – $Al(C_2H_5)_2Cl$ catalytic system, the resin yields in optimal dosage options have been exceed the results obtained when using $TiCl_4$. The type of catalyst generally has little effect on the characteristics of the resulting petroleum polymer resins.

3. The use of cyclopentadiene for modification of C_9 petroleum polymer resins at a temperature of 20 °C allows additional copolymerization of monomers with low reactivity. This allows increasing the yield of resins to 60-64%, i.e. achieving close to 100% conversion of unsaturated compounds included in the initial fraction of liquid pyrolysis products.

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