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Modification of Petroleum Bitumen by Resins Obtained from Liquid Products of Coal Coking: Composition, Properties, and Application Notice 1: Research of Raw Material Composition and Resin Synthesis

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Abstract
To obtain new modified bitumen with excellent adhesive properties, coumarone-indene resin was used. Various catalysts and raw materials obtained during the coal coking process were used to obtain CIR. The component composition of different types of light liquid coking products, which differed in the content and ratio of the main resin-forming components (styrene, indene and coumarone), was studied. It is proved that the greatest efficiency of CIR production is achieved when using fractions 140 (150)-190 (200)ºC.

***Keywords**: Bitumen; Modifier; Liquid coking products; Coumarone-indene resin; Adhesive properties.*

1. Introduction

Today, one of the most effective ways to improve the properties of bitumens is to modify them with different substances [1-3] to obtain, ultimately, the so-called polymers modified bitumen (PMB). Modification reduces the sensitivity of bitumen to changes in temperature and prolonged load, increases their cohesive strength, provides elasticity and improves low-temperature behavior. As a result, the strength, shear and crack resistance of pavements, for the manufacture of which PMB is used as a binder, increases. The resistance of such coatings to destruction and their durability increases.

The volume of application of modified bitumens is constantly growing and today accounts for about 10% of all road bitumens. Among polymer modifiers, about 75% are thermoelastoplasts (styrene–butadiene–styrene (SBS), styrene–isoprene–styrene (SIS) and styrene–ethylene/butylene–styrene (SEBS)) [4-5]. The popularity of thermoplastic elastomers is due to the combination of their elastic and thermoplastic properties. Other structurally similar polymers are also used, such as ethylene-octene copolymer [6], latex and crumb rubber [7]. They increase the cohesive strength and softening point of bitumen, give them high elasticity, improve low-temperature behavior. The main reason that restrains the growth rate of production of modified bitumens is the high cost of thermoplastic elastomers, which makes them 1.5-2.5 times more expensive than unmodified bitumens.

Reducing of the cost of modified bitumens can be achieved by two main methods:

- inexpensive additives are added into the composition of "standard" modifiers (thermoelastoplasts) [7];
- development of fundamentally new modifiers from relatively inexpensive raw materials, including secondary raw materials [7-9].

The Department of Chemical Technology of Oil and Gas Processing of the Lviv Polytechnic National University is studying the possibility of obtaining modifiers and plasticizers during the processes of oxidative processing of coal or from liquid products of its coking. These substances are the products of destruction of the organic matrix of coal [11,16,19] or compounds obtained by polymerization or polycondensation of individual liquid fractions of the coking process of coal [12,15,17,18,20,22-23]. The obtained substances used by us for modification / plasticization of bitumens are usually called resins.

It is known that CIR have good adhesive properties [24]. Therefore, among the above-mentioned substances obtained from liquid products of coking coal CIR were found as well. Their addition to bitumens can significantly increase the softening point and significantly improve the adhesive properties. The use of cheap (according to our estimates) CIR and plasticizers makes it possible to obtain high-quality PMB [13-14,21].

The above-mentioned CIRs were obtained from one type of raw material, which contained the main resin-forming components (styrene, indene and coumarone). Depending on the technology of processing volatile (gaseous and liquid) products, coke plants can produce several fractions, which can potentially be raw materials for obtaining CIR (Figure 1). It is logical to assume that the composition of these fractions may differ significantly depending on the conditions of the coking process and the directions and methods of separation of liquid products.

Thus, the raw material for the production of CIR may contain different amounts of resin-forming compounds in different ratios. Therefore, this work is devoted to the study of the composition of light liquid coking products and the possibility of obtaining CIR from them, which will be used to modify bitumens.

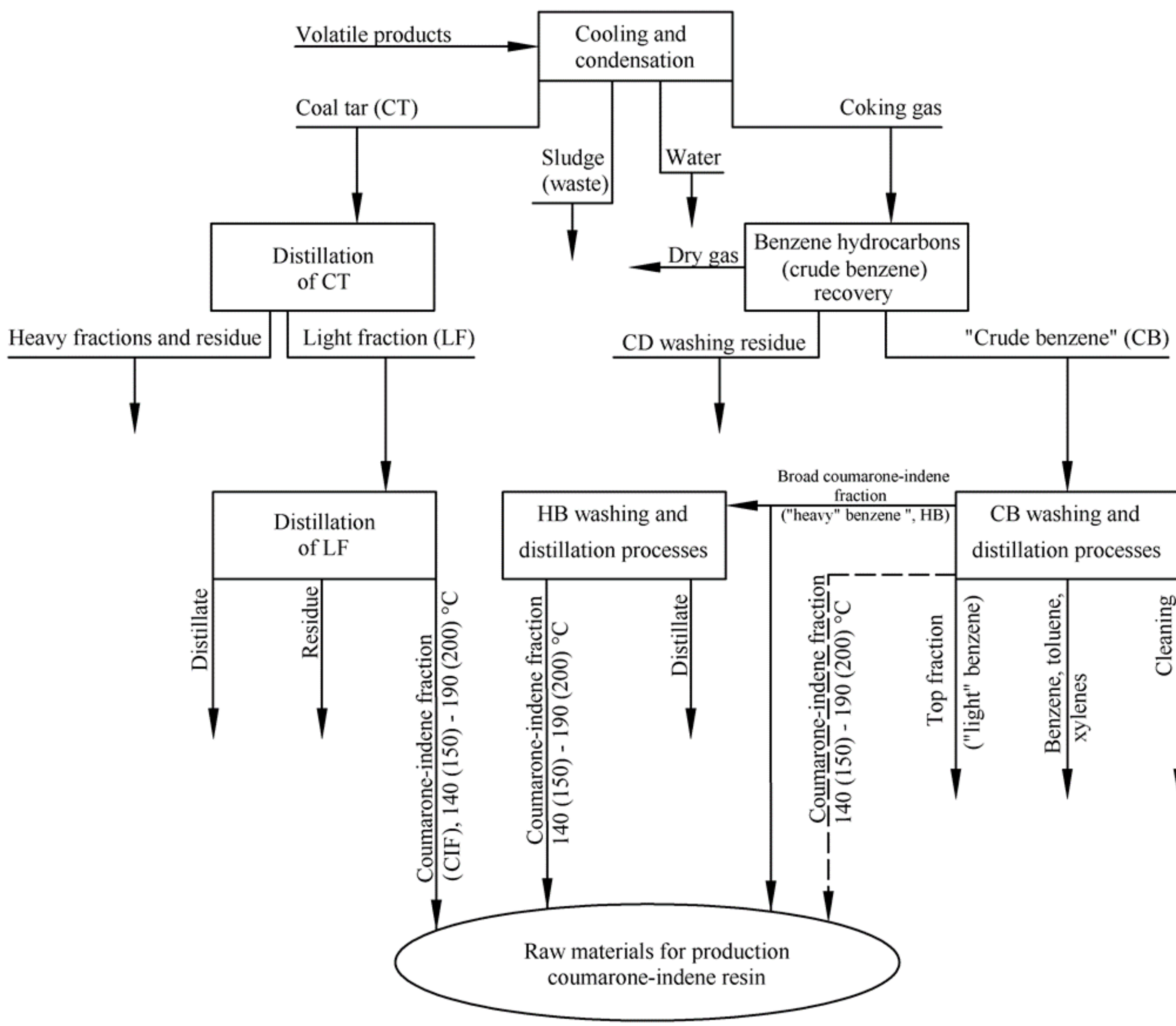


Figure 1. Current scheme of obtaining raw material for CIR synthesis

2. Experimental

2.1. Materials

Several types of non-target liquid coking products can be used to obtain CIR by ionic polymerization [13, 25, 26], as shown in Figure 1.

Therefore, five samples of three different types of non-target liquid coking products were obtained in different years, which are obtained at coke plants in Ukraine and are potential raw materials for obtaining CIR:

- raw material RM1-a wide coumarone-indene fraction (often called "heavy benzene", WCIF) from PJSC "Yasynivsky Coke Plant" (Makeyevka, Ukraine), 2013;
- raw material RM2-light fraction of coal tar (LFCT) from PJSC "Zaporizhkoks" (Zaporizhzhya, Ukraine), 2015;
- raw material RM3 – LFCT from PJSC "Zaporizhkoks" (Zaporizhzhya, Ukraine), 2017 p.;
- raw material RM4 – CIF from PJSC "Zaporizhkoks" (Zaporizhzhya, Ukraine), 2018 p.;
- raw material RM5 – WCIF from PJSC "Yuzhkoks" (Kamyanske, Ukraine),2019 p.

The fractional composition of all types of raw materials and the component composition of three different representatives of raw materials are given in Fig. 2 and in Table 1, respectively.

Analysis of the raw material shows that the light fractions of coal tar are characterized by the widest fractional composition and the lowest content of resin-forming components (styrene, coumarone, indene). This is quite logical, since LFCT is obtained by rectification of coal tar, which, in turn, is a mixture of substances condensed when cooled to 30-40 ºC volatile products of the coking process. The lighter fractional composition of light coal tar is due to the fact that at the stage of primary cooling together with the coal tar will condense part of the gasoline fractions.

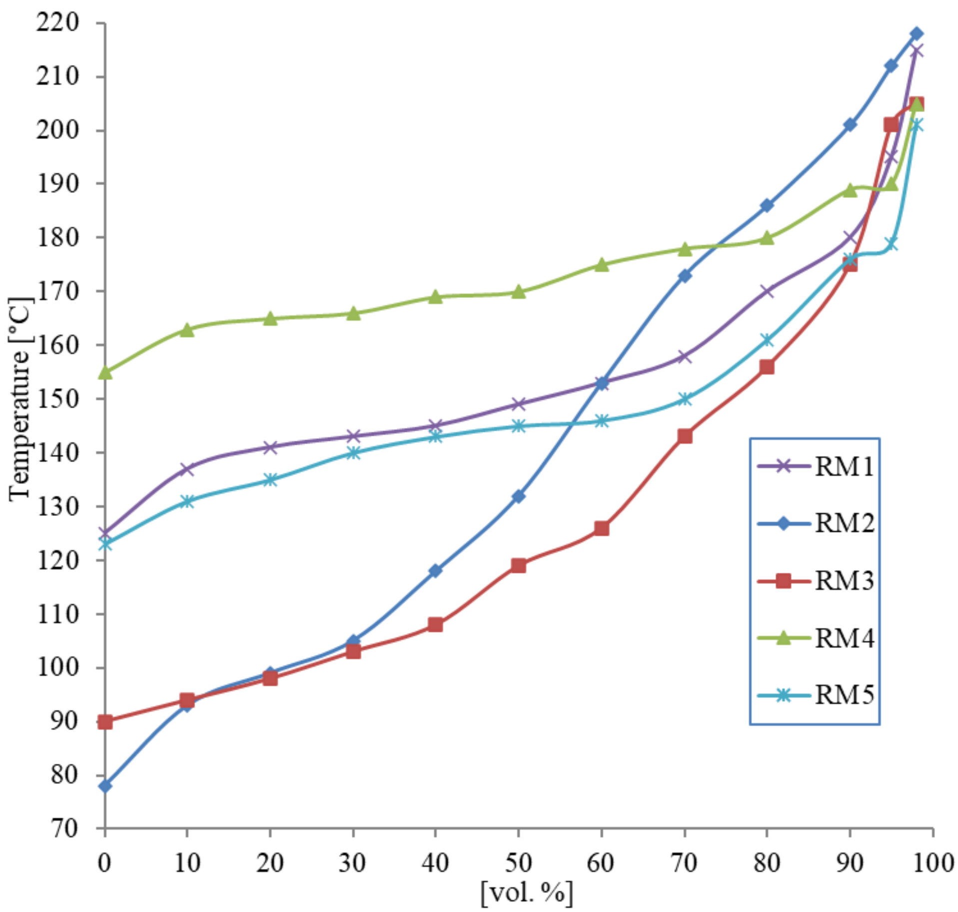
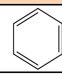
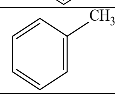
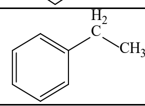
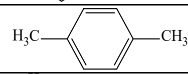
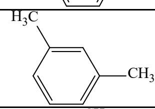
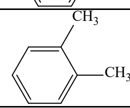
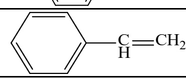
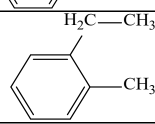
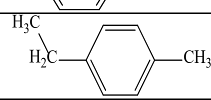
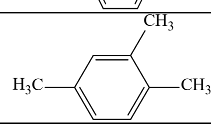
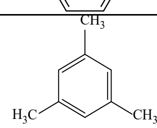
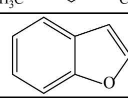
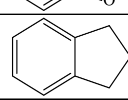
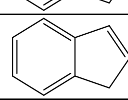
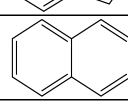
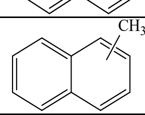


Figure 2. Fractional composition of potential raw material for obtaining CIR

Table 1. Component composition of three different types of potential raw materials for obtaining CIR

Component	Structural formula	Content for raw material [wt. %]		
		RM3	RM4	RM5
Benzene (benzol)		35.06	-	2.13
Methylbenzene (toluene)		23.78	1.23	15.28
Ethylbenzene		1.84	-	-
1,4-Dimethylbenzene (p-xylene)		17,55	8.08	39.27
1,3-Dimethylbenzene (m-xylene)				
1,2-Dimethylbenzene (o-xylene)		2.34	2.62	7.60
Ethenylbenzene (styrene)		1.26	6.72	3.61
1-Methyl-2-ethylbenzene		-	4.31	1.56
1-Methyl-4-ethylbenzene		-	-	-
1,2,4-Trimethylbenzene (pseudocumene)		1.18	7.69	2.04
1,3,5-Trimethylbenzene (mesitylene)		-	5.18	2.44
2,3-Benzofuran (coumarone)		1.29	5.74	2.05
2,3-Dihydroindene (indane)		4.37	2.63	-
Benzocyclopentadiene (indene)		3.94	44.41	19.65
Naphthalene (naphthalin)		1.79	6.86	2.51
Methylnaphthalins		3.56	-	-
Other hydrocarbons[1] and unidentified compounds	–	2.04	4.53	1.86
Total	–	100.00	100.00	100.00
Quantity of resin-forming[2] components [wt. %]	–	6.49	56.87	25.31

Component	Structural formula	Content for raw material [wt. %]		
		RM3	RM4	RM5
The content of styrene in resin-forming[2] components [wt. %]	–	19.41	11.82	14.26
The content of coumarone in resin-forming[2] components [wt. %]	–	19.88	10.09	8.10
The content of indene in the resin-forming[2] components [wt. %]	–	60.71	78.09	77.64

[1]Components, the content of which in all samples did not exceed 1%. [2]Styrene, coumarone, indene

WCIF ("heavy benzene") is a residue obtained at the stage of distillation of "crude" (technical) benzene. The latter, in turn, is removed by absorption from products that have not condensed to produce coal tar (see Figure 1). CIF is a product obtained at the stage of distillation of "crude" benzene or WCIF. Based on the production technology, it is quite logical that the fractional compositions of WCIF and CIF are narrower, and the content of resin-forming components is higher than in LFCT.

The main component of resin-forming substances is indene, which is 60-80% of the mass. of their total number.

2.2. Methods of conducting experiments

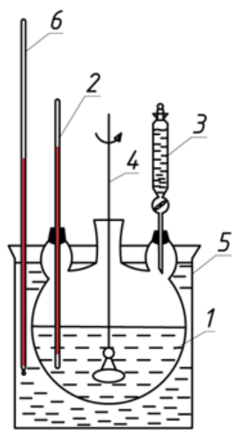


Figure 3. Conditional scheme of laboratory installation for CIR synthesis: 1 - round bottom three-necked flask; 2, 6 - thermometer; 3 - dividing funnel / dispenser; 4 - mixing device; 5 – thermostat

The synthesis of CIR was carried out according to the following method. The raw material was pre-treated to dry and remove the pyridine bases with 72% sulfuric acid, which in turn reduced catalyst consumption and increased CIR yield and softening point. Subsequently, the prepared feedstock was placed in a reactor, the process conditions (duration and temperature, amount of catalyst) were monitored, and polymerization was performed with stirring. The resulting resin was washed with water until neutral. Unreacted raw materials were distilled from CIR by vacuum distillation. The resin yield was determined by weighing the raw material and CIR. The conditional scheme of the laboratory installation for CIR synthesis is given in Fig. 3.

2.3. Analysis of starting materials and products

Developmental gas adsorption chromatography was used to determine the component composition of the raw material and individual fractions. Two chromatographic systems with flame ionization detectors were used:

- on the basis of the chromatograph "Chromatek-crystal 5000.2". The separation of the components was carried out on a capillary column with a length of 50 m with a deposited liquid phase of PON (paraffins, olefins, naphthenes, aromatics). The carrier gas is helium. Temperature programming - from 40 to 180°C. Error - 0.01% vol;
- based on the chromatograph "Crystal 2000M". Separation of the components was carried out on a column 3 m long, filling the column-"Chromaton" with 20% polyphenyl ether 5f4e. The carrier gas is helium. Temperature programming from - 145 to 250°C. Error 0.01% vol.

Chromatograms were analyzed using the software "Chromatek-analyst 1.5" and "Chromatek-gasoline".

3. Results and Discussion

It is known that unsaturated (resin-forming) compounds that are part of the raw material can be cooligomerized by both radical (thermal [27] and initiated [28-30] cooligomerization) and ionic mechanism (acid catalysis).

The last variant is mainly widespread in the industry; Lewis, Bronsted acids and mixtures thereof are used as catalysts. The literature describes quite a few ways to obtain CIR in this way, the chemistry and mechanism of their production [27].

According to the modern theory of the mechanism of carbation reactions, the products of cooligomerization of the indene-coumarone fraction must retain at least one double bond, which is confirmed by their ability to attach bromine or iodine. In terms of chemical structure, they may consist of:

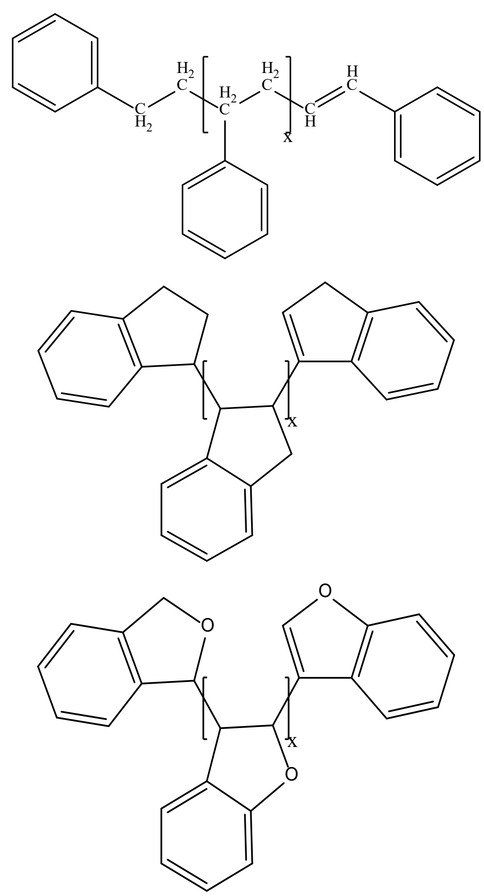
1) the same type of links (oligomers or polymers, Scheme 1);
2) different units (copolymers or cooligomers, Scheme 2).

It is also possible to form branched structures with several unsaturated bonds, for example, by attaching a carbocation to an already formed macromolecule or participating in the reaction of diene hydrocarbons contained in the raw material. For example, the following is a possible structure of a branched CIR structure consisting of different monomer units (Scheme 2).

a

b

c



Scheme 1. Structural formulas of polystyrene (a), polyindene (b), polycoumarone (c)

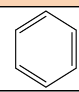
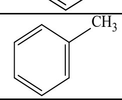
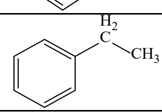
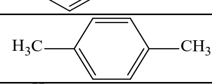
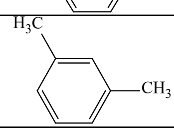
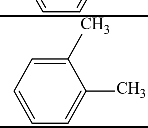
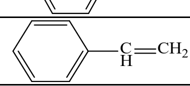
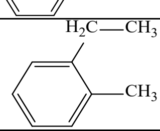
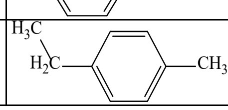
As can be seen from the above structures, the polymerization products have at least one unsaturated bond at the end of the chain due to which they can form chemical/physico-chemical bonds with the bitumen and / or the coating surface on which the bitumen is applied. In addition, resins can have different molecular weights, ratios and locations of structural units. All this will significantly affect the ability of these resins to dissolve in bitumen, to form independent spatial structures in them, to change the rheological, cohesive and adhesive properties of bitumen, and so on. It is also clear that the structural and spatial formulas of the resins will depend on the conditions of production and composition of raw materials.

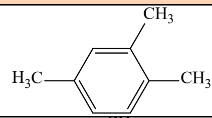
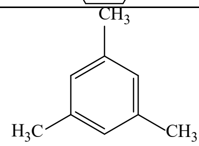
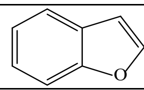
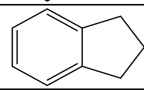
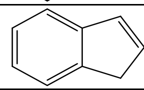
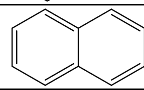
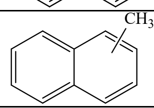
It is established [13-14] that the modifying properties of CIR (in terms of improving the characteristics of bitumen, primarily adhesion) are directly proportional to TPC: increasing TPC improves its modifying properties. In [31-35] it was also found that to achieve the appropriate quality indicators of polymer modified bitumen (PMB) it is desirable to use CIR with a softening point of at least 130-140ºC. The use of resins with lower TPC has a less significant positive effect on the softening point and adhesion properties of PMB, including at low temperatures. Therefore, the task of research was to obtain resins with a maximum SPR (with a satisfactory yield) of all listed in Sec. 2 types of raw materials.

3.1. Selection of raw materials for obtaining CIR

It is believed that the optimal content of resin-forming components in the raw material is 30-40% of the mass.[14, 27]. To increase the content of the necessary components, it is advisable to use Fr. 140(150) - 190(200)ºC, which is explained by the boiling points of styrene (145 ºC), coumarone (171ºC) and indene (183ºC). Therefore, from the raw materials (Table 1 and Fig. 2) were allocated narrower fractions, the characteristics of which are given in Table 2 and 3. In addition, the fractions of raw materials RM2 to analyze after storage for 2 years in conditions close to storage in industry.

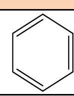
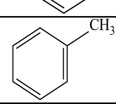
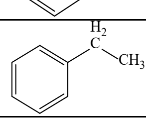
Table 2. Component composition of fractions 140-190 (200)°C

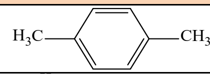
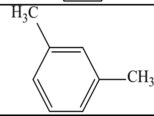
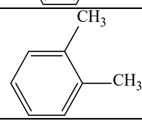
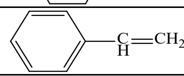
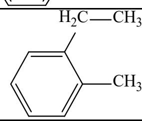
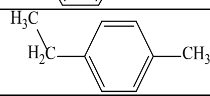
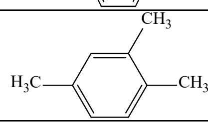
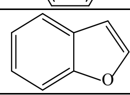
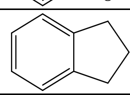
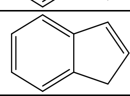
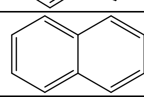
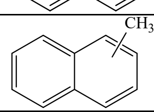
Component	Structural formula	Content [wt. %]				
		RM1-140-190[3]	RM2-140-190[4]	RM3-140-190-2017[5]	RM4-140-190[6]	RM5-140-200[7]
Benzene (benzol)		0.48	4.05	4.13	1.84	-
Methylbenzene (toluene)		4.44	17.01	17.82	2.21	7.34
Ethylbenzene		1.98	1.28	2.97	–	-
1,4-Dimethylbenzene (p-xylene)		3.79	3.16	26.57	12.38	39.40
1,3-Dimethylbenzene (m-xylene)		23.82	19.93			
1,2-Dimethylbenzene (o-xylene)		5.15	3.48	3.86	4.05	8.26
Ethenylbenzene (styrene)		18.13	8.81	3.17	9.68	3.86
1-Methyl-2-ethylbenzene		1.46	0.91	2.12	5.03	2.11
1-Methyl-4-ethylbenzene			0.97	2.00	–	-

Component	Structural formula	Content [wt. %]				
		RM1-140-190[3]	RM2-140-190[4]	RM3-140-190-2017[5]	RM4-140-190[6]	RM5-140-200[7]
1,2,4-Trimethylbenzene (pseudocumene)		4.31	2.16	2.98	8.56	2.69
1,3,5-Trimethylbenzene (mesitylene)		–	–	–	5.29	–
2,3-Benzofuran (coumarone)		1.65	3.50	3.20	6.34	2.69
2,3-Dihydroindene (indane)		22.15	22.82	9.18	2.58	-
Benzocyclopentadiene (indene)				9.43	36.38	27.24
Naphthalene (naphthalin)		2,08	2,21	2,54	2.61	3.54
Methylnaphthalins		–	6,45	7.56	–	-
Other hydrocarbons[1] and unidentified compounds	–	10.56	3.26	2.47	3.05	2.87
Total	–	100.00	100.00	100.00	100.00	100.00
Quantity of resin-forming[2] components [wt. %]	–	40.93[8]	23.72[9]	15.80	52.40	33.79
The content of styrene in resin-forming[2] components [wt. %]	–	44.30	37.14	20.07	18.47	11.42
The content of coumarone in resin-forming[2] components [wt. %]	–	4.03	14.76	20.25	12.10	7.96
The content of indene in the resin-forming[2] components [wt. %]	–	51.67	48.10	59.68	69.43	80.62

[1]Components, the content of which in all samples did not exceed 1%. [2]Styrene, coumarone, indene. [3]Fr. 140-190ºC from raw materials RM1. [4]Fr. 140-190ºC from raw materials RM2. [5]Fr. 140-190ºC from raw materials RM2, analyzed after storage for 2 years (in 2017). [6]Fr. 140-190ºC from raw materials RM4. [7]Fr. 140-200ºC from raw materials RM5. [8] Considering the composition of a similar WCIF (RM5-140-200), the content of indane 1 wt. %. [9]Considering the composition of RM2-140-190-2017, the content of indane 0.5 × 22.82 = 11.41wt. %.

Table 3. Component composition of fractions 150-190°C

Component	Structural formula	Content [wt. %]		
		RM2-150-190[3]	RM2-150-190[4]	RM3-150-190[5]
Benzene (benzol)		1.98	1.81	1.27
Methylbenzene (toluene)		12.08	13.15	10.34
Ethylbenzene		2.26	2.78	2.38

Component	Structural formula	Content [wt. %]		
		RM2-150-190[3]	RM2-150-190[4]	RM3-150-190[5]
1,4-Dimethylbenzene (p-xylene)		22.78	26.10	25.73
1,3-Dimethylbenzene (m-xylene)				
1,2-Dimethylbenzene (o-xylene)		3.43	3.95	4.24
Ethenylbenzene (styrene)		9.06	3.26	2.51
1-Methyl-2-ethylbenzene		2.35	2.45	2.35
1-Methyl-4-ethylbenzene		2.13	2.24	2.59
1,2,4-Trimethylbenzene (pseudocumene)		3.38	3.47	3.41
2,3-Benzofuran (coumarone)		4.07	3.68	3.55
2,3-Dihydroindene (indane)		24.26	10.84	12.85
Benzocyclopentadiene (indene)			11.20	11.05
Naphthalene (naphthalin)		2.64	3.12	4.00
Methylnaphthalins		7.21	9.15	10.58
Other hydrocarbons[1] and unidentified compounds	–	2.37	2.80	3.15
Total	–	100.00	100.00	100.00
Quantity of resin-forming[2] components [wt. %]	–	25.26	18.14	17.11
The content of styrene in resin-forming[2] components [wt. %]	–	35.87	17.97	14.67
The content of coumarone in resin-forming[2] components [wt. %]	–	16.11	20.29	20.75
The content of indene in the resin-forming[2] components [wt. %]	–	48.02	61.74	64.58

[1]Components, the content of which in all samples did not exceed 1%. [2]Styrene, coumarone, indene. [3]Fr. 150-190ºC from raw materials RM2. [4]Fr. 150-190ºC from raw materials RM2, analyzed after storage for 2 years (in 2017). [5]Fr. 150-190ºC from raw materials RM3. [6] Considering the composition of RM2-150-190-2017, the content of indan 0.5 × 24.26 = 12.13 wt. %.

As can be seen from the obtained data, narrow distillates are characterized by a much higher content of RC than the original broad fractions, which were selected at coke plants in Ukraine (except for the use of CIF-RM4). Raw material RM4 is a fraction already obtained in the industry, which boils in the range of 150-190ºC with a very high content of RC. Therefore, during the re-distillation of this fraction, the amount of low-boiling RC (styrene and coumarone) increases slightly, and the content of indene and RC in general decreases. Also in the case of use as a raw material WCIF and LFCT content of RC in Fr. 150-190ºC was greater than in Fr. 140-190ºC.

When distilling LFCT (RM2 and RM3) in any case failed the obtained raw material with the desired content of RC (30-40% wt.).

It should also be noted that in the case of storage of raw materials at the enterprise decreases the content of RC, especially styrene (see Table 2, characteristics RM2-140-190 and RM2-140-190-2017). This is explained by the fact that during storage of raw materials at the plant, even at ambient temperature, copolymerization of unsaturated compounds occurs.

In all types of raw materials and their narrow fractions among the resin-forming components is dominated by indene, the content of which (based on the RC) is 50-80% of the mass.

3.2. Obtaining of CIR

The synthesis of resins from narrow fractions was carried out under conditions close to the optimal ones specified in [13]. $AlCl_3$ or $TiCl_4$ were used as catalysts. The results of obtaining resins from Fr. 140-190 (200) ° C and CIF (RM4) are given in Table 4.

Table 4. Characteristics of CIR (Synthesis conditions: temperature – 40ºC, duration – 40 min., catalyst concentration $TiCl_4$ – 3.0 wt. %)

Index	Value for resin				
	RM1-140-190	RM2-140-190	RM3-140-190	RM4	RM5-140-200
Yield of resin [wt. %]	39.2	25.8	12.4	52.7	27.0
SPR [°C]	124	97	60	139	130

The results, given in Table 4, prove that the yield of resins is proportional to the content of RC in the raw material.

From the fractions distilled from RM1, RM4 and RM5 it is possible to obtain resins with Tpc> 120-130ºC. Comparing the softening point of the resins obtained from RM1-140-190 and RM5-140-200, we can conclude that, even with a lower content of RC, but a higher ratio of indene: (styrene + coumarone), it is possible to obtain resins with higher SPR .

It should be noted that when using RM4-140-190, the content of RC in which was 52.4% wt., It is technically difficult to obtain CIR in the laboratory, because the reaction often becomes thermo-uncontrolled, which leads to a sharp increase in temperature and boiling of the reaction mixture. It can be assumed that a similar effect will be observed in the industry. This is due to the high content of RC. Therefore, it is possible to recommend a permissible content in the raw material of the IC not more than 30-40% wt., As indicated in [14, 27].

The results, given in Table 3, allow us to conclude that, despite the same boiling point, with RM2-140-190, CIR is obtained with a higher softening point and yield than with RM3-140-190, due to the higher content of unsaturated reactive components in with RM2-140-190. In both cases, it is not possible to obtain a CIR with the recommended SPR (at least 120-130 ºC).

According to experimental data (see Tables 2 and 3), narrower fractions are characterized by a higher content of unsaturated components. Therefore, the next step was to obtain CIR from fractions with a boiling range of 150-190°C, which were distilled off from LFCT. The research results are given in Table 5.

As can be seen from the results, the narrowing of the fractional composition allows to increase the yield and softening point of CIR for both fractions 150-190 ºC (compared with the case of obtaining resins from fr. 140-190ºC), especially RM3-140-190, which is evidence effectiveness of this method. In this case, as in the previous case, RM3-140-190 is the worst raw material in terms of quality of the obtained CIR.

Table 5. Characteristics of CIR (synthesis conditions: temperature – 40ºC, duration – 40 min., catalyst concentration $TiCl_4$ – 3.0 wt. %)

Index	Value for resin	
	RM2-150-190	RM3-150-190
Yield of resin [wt. %]	28.4	17.2
SPR [°C]	114	88

In addition to the proposed titanium (IV) chloride, Bransted (H_2SO_4) and Lewis acids ($SnCl_4$, $SbCl_5$, $AlCl_3$, BF_3, etc.) can also be catalysts in the process of obtaining indene-coumarone resins [13, 27]. As an alternative to $TiCl_4$, we have choose aluminum chloride (III). The results of the relevant studies are given in Table 6.

Table 6. Characteristics of CIR (synthesis conditions: temperature – 40ºC, duration – 40 min., catalyst concentration $AlCl_3$ – 3.0 wt. %)

Index	Value for resin	
	RM2-150-190	RM3-150-190
Yield of resin [wt. %]	26.2	15.2
SPR [°C]	95	85

The yield and quality of CIR, the results of the synthesis of which are given in Table 4-6, it can be stated that the catalyst $AlCl_3$, compared to titanium (IV) chloride, is less active in the studied process, which is confirmed by the lower yield and softening point of the obtained coumarone-indene resins.

From previous studies [11-13] it is known that increasing the amount of catalyst makes it possible to obtain a resin with a higher SPR. The results of the experiments are given in Table 7 and 8.

Table 7. Characteristics of CIR (synthesis conditions: temperature – 40ºC, duration – 40 min., catalyst concentration $TiCl_4$ – 6.0 wt. %)

Index	Value for resin	
	RM2-150-190	RM3-150-190
Yield of resin [wt. %]	26.4	17.7
SPR [°C]	128	117

Table 8. Characteristics of CIR (Synthesis conditions: temperature – 40 ºC, duration – 40 min., Catalyst concentration $AlCl_3$ – 6.0 wt. %)

Index	Value for resin	
	RM2-150-190	RM3-150-190
Yield of resin [wt. %]	26.50	17.1
SPR [°C]	112	94

Increasing the amount of catalyst doubles the quality of the resins and may even increase the yield (in the case of RM3-150-190). This trend is characteristic for both $TiCl_4$ (Table 7) and $AlCl_3$ (Table 8).

In the case of using $TiCl_4$ as a catalyst. even with RM3-150-190 it is possible to obtain a resin with satisfactory characteristics (TPC is close to 120ºC).

Based on the research. it can be concluded that coumarone-indene resin was obtained from the light fraction of coal tar. To achieve a high yield of resin and its satisfactory softening point. it is advisable to use raw materials of narrower fractional composition and increased amounts of $TiCl_4$ catalyst. compared with the conditions proposed in [31-35] to obtain CIR from indene-coumarone fractions isolated from "heavy" benzene.

Although coumarone-indene resins of the desired quality were obtained from all types of raw materials. the behavior of different types of raw materials differed (primarily. differences in yields and SPRs were observed between the fractions obtained from "crude" benzene and coal tar). Therefore. further research will be devoted to the study of the composition of different CIR and the possibility of effective modification of petroleum bitumen by resins.

4. Conclusions

Liquid fractions. which are obtained at coke plants of Ukraine and can be used for the production of CIR. differ in the content of resin-forming components (styrene. coumarone. indene) and their ratio. The most effective raw materials for the production of resins that can be used as modifiers of petroleum bitumen are coumarone-indene fractions obtained from "crude" benzene.

From all types of liquid raw materials produced during the coking of coal and containing styrene. coumarone and indene. it is possible to obtain CIR. which can be used as modifiers of road petroleum bitumen. The optimal content of RC should be considered 30-40% of the mass. At their higher content. the cooligomerization reactions become thermocontrolled; at a significantly lower content of RC to obtain resins with SPR ≥ 120ºC it is necessary to increase the amount of catalyst to 6% of the mass. on raw materials.

Abbreviations

CIR	*coumarone-indene resin;*
PMB	*polymers modified bitumen;*
SPR	*softening point of these resins (ring&ball method);*
LFCT	*light fraction of coal tar;*
CT	*coal tar;*
CIF	*coumarone-indene fraction;*
LP	*unreacted components that remained after the polymerization reactions;*
RC	*resin-forming components;*
RM	*raw materials.*

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