

Synthesis of condensed polynuclear aromatic resin from furfural extract oil of reduced-pressure route II

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Abstract: As an industrial byproduct of oil refining, furfural extract oil from reduced-pressure route II with high aromatic content was used to prepare heat-resistant condensed polynuclear aromatic (COPNA) resin for the first time. The basic properties of furfural extract oil and the resultant COPNA resin were characterized by infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$), thermogravimetric analysis (TGA) and elemental analysis (EA). The result showed that heat treated furfural extract oil was successfully used for the synthesis of heat-resistant COPNA resin. The average structural parameters of raw materials and prepared resin were calculated by the improved Brown-Ladner method, and the averaged molecular structure of the resin was obtained. The reaction mechanism for the synthesis of COPNA resin was suggested as an acid-catalyzed positive ion type polymerization.

Key words: Furfural extract oil, reduced-pressure route II, COPNA resin, synthesis, reaction mechanism

1 Introduction

The synthesis of COPNA resin was firstly reported by Otani (Otani et al, 1986). As a novel heat-resistant material with good lubricity, mechanical properties and mouldability, this resin has attracted considerable attention for its potential applications (Kusakabe et al, 1998; Li et al, 2010; Lin et al, 2010a; 2010b; Tanemura et al, 2011; 2012; Zhao et al, 2008). In the early stages, raw materials for the preparation of COPNA resin were confined to pure aromatic substances (Nakajima et al, 1995; Nawa, 1996; Nawa and Ohkita, 1997). Recently, a number of similar raw materials including coal derived and petroleum based mixtures have been successfully used to prepare COPNA resin (Guo et al, 2002; Li et al, 2008; Shi et al, 2012; Wu et al, 2012; 2012). Furfural extract oil from reduced-pressure route II, commonly used as fuel oil for boilers or for the manufacture of synthetic rubber, is a byproduct of oil refining. With a high aromatic content, narrow molecular weight distribution and low content of heavy metals, furfural extract oil is theoretically considered as an ideal candidate raw material to prepare COPNA resin.

In this work, furfural extract oil from reduced-pressure route II was firstly heated at atmospheric pressure to remove its volatile components. Then, COPNA resin was eventually synthesized through the reaction of the thermally condensed oil and the cross-linking agent (1, 4-benzenedimethanol, PXG), which was catalyzed by p-toluene sulfonic acid (PTS). The resultant resin as well as the raw materials

were characterized by elemental analysis (EA), infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$) and thermogravimetric analysis (TGA).

2 Experimental

2.1 Raw materials

Furfural extract oil from reduced-pressure route II was provided by Jiangshan Polymer Material Company, China. PXG (AR) and PTS (AR) were both purchased from SINOPHARM Chemical Reagent Company, China. Toluene was obtained from Tianjin Chemical Reagent Company, China. Quinoline was purchased from Tingxin Chemical Reagent Company, China.

2.2 Heat treatment of furfural extract oil from reduced-pressure route II

Furfural extract oil from vacuum second side-cut was added into a reaction kettle equipped with a thermometer and mechanical stirrer. The reaction kettle was heated to 420 °C at 2 °C/min in a nitrogen flow of 50 mL/min and then kept for 3 h. A small amount of the light fraction of furfural extract oil was found to have evaporated after heat treatment and the thermally condensed oil was obtained.

2.3 Preparations of COPNA resin

The thermally condensed oil, PXG and PTS (with a weight ratios of 75:20:5) were fully mixed in a reactor, and then the mixture was stirred and heated in a nitrogen flow of 40 mL/min. The reactor was heated to 130 °C at 5 °C/

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min and kept for 1 h, then heated to 150 °C and held until a solidified COPNA resin was observed. It is noteworthy that the viscosity of this system increased gradually, indicating that the degree of polymerization increased gradually during the reaction.

2.4 Characterization

The prepared COPNA resins and the raw materials were analyzed by TGA, FT-IR, NMR and elemental analysis.

For TGA measurements, about 10 mg sample was placed in a platinum crucible of a SHIMADZU DTG-60 thermogravimetric analyzer, and heated from room temperature to 900 °C at a heating rate of 10 °C/min under a nitrogen flow of 50 mL/min.

FT-IR spectra of the samples were obtained with a Shimadzu 8400S FT-IR spectrometer in transmittance mode. The scan frequency of each spectrum was 15 s⁻¹ with a resolution of 0.85 cm⁻¹.

A BRUKER AV500 ¹H-NMR spectrometer was used to characterize the state of different hydrogen in prepared COPNA resins and the raw materials. The solvent used was chloroform, the internal standard label was trimethylphenylsilane, the sweep length was 10,000 Hz, and the resonance frequency was 500 MHz.

Elemental analysis was performed by the Vario EL organic element analyzer. The structural data of the obtained COPNA resin and raw materials was calculated by the Brown-Ladner formula (Wu et al, 2012a; 2012b).

3 Results and discussion

3.1 Properties of furfural extract oil and thermally condensed oil

The basic properties of furfural extract oil and its thermally condensed oil are given in Table 1. We can see that the average molecular weight of furfural extract oil was 273, the saturate content was 11.1wt%, while the aromatics content was 81.6wt%. After heat treatment, the average molecular weight was increased to 338, the saturate content was reduced

Table 1 Properties of furfural extract oil and its thermally condensed oil

Properties	Furfural extract oil	Thermally condensed oil
M	273	338
CR, wt%	8.9	18.2
QI, wt%	0.1	0.2
TI, wt%	0.3	0.6
(TI-QI), wt%	0.2	0.4
Saturates, wt%	11.1	3.7
Aromatics, wt%		
Light	21.5	4.1
Middle	37.9	34.3
Heavy	22.2	43.8
Others, wt%	7.3	14.1

Notes: M, average molecular weight; CR, carbon residue ratio; TI, toluene insoluble; QI, quinoline insoluble.

to 3.7wt% and the light aromatics content was decreased to 4.1wt%. However, there was a remarkable increase in heavy aromatics, from 22.2wt% of furfural extract oil to 43.8wt% of thermally condensed oil. TI and QI values of thermally condensed oil were both higher than those of furfural extract oil. These results showed that polymerization reactions took place during the process of heat treatment.

Table 2 shows the elemental analysis of furfural extract oil and thermally condensed oil. After the thermal condensation of furfural extract oil, the total content of other elements was reduced from 2.6wt% to 1.7wt%, the value of C/H increased from 1.10 to 1.16, and the f_A data increased from 0.68 to 0.76. The results indicated that some ingredients in furfural extract oil can be removed by heat treatment and condensation in this process.

Table 2 Elemental analysis of furfural extract oil and its thermally condensed oil

Samples	Elements, wt%					C/H	f_A
	C	H	N	O	Others		
Furfural extract oil	89.5	6.8	0.3	0.8	2.6	1.10	0.68
Thermally condensed oil	90.4	6.5	0.6	0.8	1.7	1.16	0.76

3.2 Properties of COPNA resin

3.2.1 Basic properties of COPNA resin

Table 3 shows the basic properties of the obtained COPNA resin. Tables 1 and 3 indicate that the residual carbon ratio was dramatically increased from 18.2wt% in thermally condensed oil to 32.6wt% in the COPNA resin. Both TI and QI values were also greatly increased, and the TI-QI value was increased significantly from 0.4 wt% in the thermally condensed oil to 12.4wt% of COPNA resin. The TI-QI value is a critical parameter that determines the binding performance, and resin with a TI-QI value of >8.0wt% is

Table 3 Properties of COPNA resin

Properties	Values
M	1412
CR, wt%	32.6
QI, wt%	5.6
TI, wt%	17.9
(TI-QI), wt%	12.4
Softening point, °C	110
C, wt%	89.1
H, wt%	6.1
N, wt%	0.4
O, wt%	1.5
Others, wt%	2.9
C/H	1.22
f_A	0.77

deemed suitable for industrial application as a binder. In addition, the average molecular weights in Tables 1 and 3 showed that the average degree of polymerization was around 3.

3.2.2 FT-IR analysis

The FT-IR spectra of furfural extract oil, thermally condensed oil and COPNA resin are shown in Fig. 1. Peaks at 3,420-3,550 cm^{-1} in Fig. 1 were attributed to N-H stretching vibration and O-H stretching vibration. Peaks at 3,046 cm^{-1} and 1,602 cm^{-1} were attributed to aromatic C-H and C=C stretching vibrations. The peak at 1,455 cm^{-1} was from C-H bending vibration. These peaks clearly revealed the existence

of the elements C, H, N and O, as well as the corresponding chemical bonds they formed. The peaks at 750 cm^{-1} , 810 cm^{-1} and 872 cm^{-1} were possibly generated by the out-of-plane bending vibrations of 2, 3, 4-aromatic C-H. These results confirmed the existence of various forms of aromatic substitution reaction.

In contrast with peaks in Fig.1(a), peaks at 2,920 and 2,854 cm^{-1} attributed to the C-H stretching vibration in $-\text{CH}_2-$ were weakened in Fig. 1(b). The peaks between 900 cm^{-1} and 650 cm^{-1} in Fig. 1(b) (such as 875 cm^{-1} , 810 cm^{-1} and 748 cm^{-1}) attributed to out-of-plane bending vibration of C-H in aromatics were weaker than those of Fig. 1(a). These changes indicated that condensation of furfural extract oil occurred during heat treatment.

In Fig. 1(c), the absorption peaks around 2,920 and 2,855 cm^{-1} were stronger than those of Fig. 1(b), indicating the occurrence of the cross-linking reactions between PXG and thermally condensed oil. The peaks in Fig. 1(c) at 1,600 cm^{-1} attributed to C=C stretching vibration and the peaks between 900 cm^{-1} and 650 cm^{-1} belonged to out-of-plane bending vibration of C-H in aromatics were much stronger than those of Fig. 1(b), indicating that the cross-linking reactions changed the types of aromatic substitution.

3.2.3 $^1\text{H-NMR}$ analysis

The $^1\text{H-NMR}$ spectra of furfural extract oil, thermally condensed oil and COPNA resin are shown in Fig. 2. The large peaks between δ 7.0 and δ 9.0 were attributed to the absorption resonance of hydrogen in aromatic rings. Fig. 2 also presents α -H absorption resonance peaks between δ 2.0 and δ 4.0, β -H absorption resonance peaks between δ 1.0 and δ 2.0, as well as γ -H absorption resonance peaks between δ 0.5 and δ 1.0. The data of Fig. 2 is summarized in Table 4, where H_α means the weight ratio of α - CH_3 , α - CH_2 and α -CH in aromatic ring (i.e. the weight ratio of α -hydrogen to the total hydrogen in weight). H_A refers to the weight ratio of aromatic H in aromatic rings. Similarly, H_β and H_γ refer to the weight ratio of β - CH_2 and β -CH hydrogen and γ - CH_3 hydrogen in the aromatic rings, respectively.

It is noteworthy that the content of H_A increased from 29.6% of furfural extract oil to 43.9% of thermally condensed oil, while there was a distinct decrease in the content of H_β . This was because β -H was mostly located on side-chains, and the decrease in β -H demonstrated side-chain cleavage and an increase in polymerization degree, which was in accordance with the analysis of aromatics and the results of FTIR. The content of H_α increased significantly after synthetic reaction, indicating that the aromatics connected with $-\text{CH}_2-$ of PXG.

3.3 Mechanism of COPNA resin synthesis

Based on the results of FTIR, $^1\text{H-NMR}$, elemental analysis and average molecular weight analysis of furfural extract oil, thermally condensed oil and COPNA resin, the average structural parameters, including C_T , H_T , f_A , H_{AU}/C_A , σ , R_T , R_A , R_N , and C_R , were obtained by the improved Brown-Ladner method. The obtained average structure parameters are shown in Table 5, in which the S, O and N levels were negligible. The reaction mechanism and averaged molecular structure of COPNA resin are as follows:

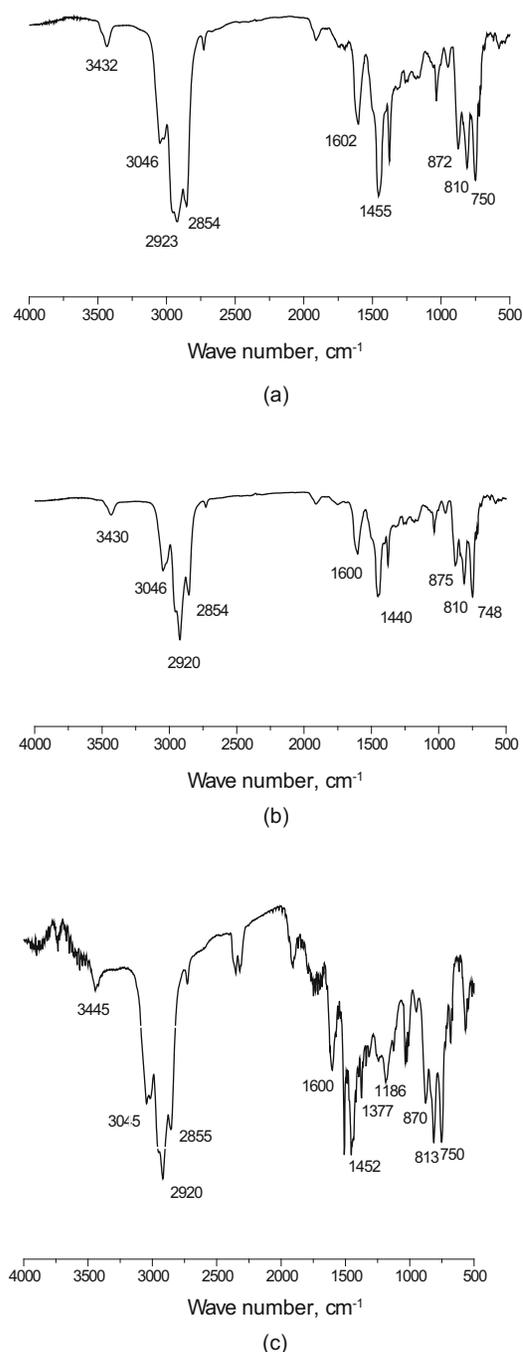


Fig. 1 FT-IR spectra of furfural extract oil (a), thermally condensed oil (b) and COPNA resin (c)

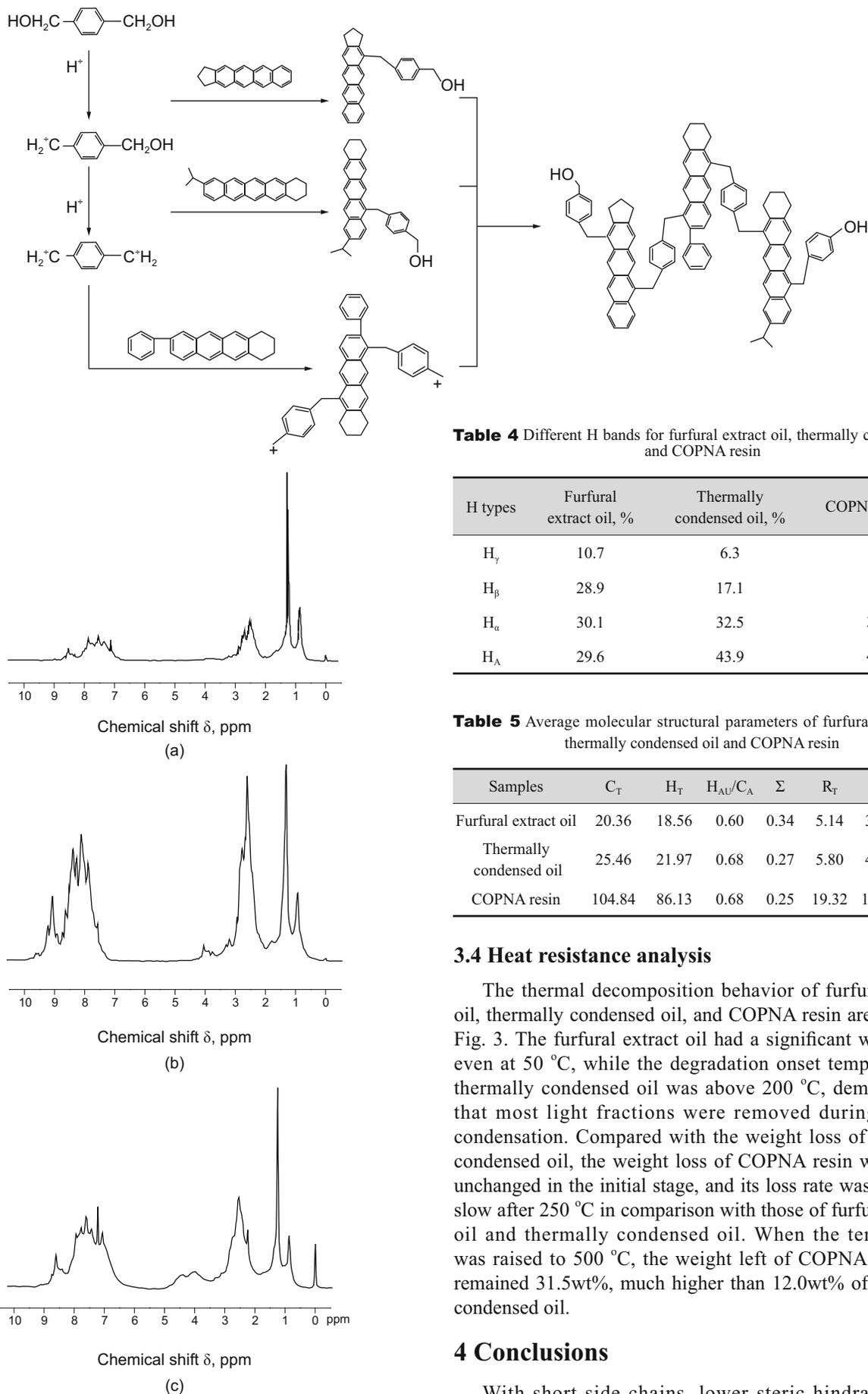


Fig. 2 ¹H-NMR spectra of furfural extract oil (a), thermally condensed oil (b) and COPNA resin (c)

Table 4 Different H bands for furfural extract oil, thermally condensed oil and COPNA resin

H types	Furfural extract oil, %	Thermally condensed oil, %	COPNA resin, %
H _γ	10.7	6.3	4.7
H _β	28.9	17.1	16.2
H _α	30.1	32.5	36.0
H _A	29.6	43.9	43.0

Table 5 Average molecular structural parameters of furfural extract oil, thermally condensed oil and COPNA resin

Samples	C _T	H _T	H _{AU} /C _A	Σ	R _T	R _A	R _N
Furfural extract oil	20.36	18.56	0.60	0.34	5.14	3.00	2.14
Thermally condensed oil	25.46	21.97	0.68	0.27	5.80	4.34	1.46
COPNA resin	104.84	86.13	0.68	0.25	19.32	15.87	3.23

3.4 Heat resistance analysis

The thermal decomposition behavior of furfural extract oil, thermally condensed oil, and COPNA resin are shown in Fig. 3. The furfural extract oil had a significant weight loss even at 50 °C, while the degradation onset temperature of thermally condensed oil was above 200 °C, demonstrating that most light fractions were removed during thermal condensation. Compared with the weight loss of thermally condensed oil, the weight loss of COPNA resin was almost unchanged in the initial stage, and its loss rate was relatively slow after 250 °C in comparison with those of furfural extract oil and thermally condensed oil. When the temperature was raised to 500 °C, the weight left of COPNA resin still remained 31.5wt%, much higher than 12.0wt% of thermally condensed oil.

4 Conclusions

With short side chains, lower steric hindrance, high aromatic content and purity, furfural extract oil from reduced-pressure route II is selected as raw material for the preparation

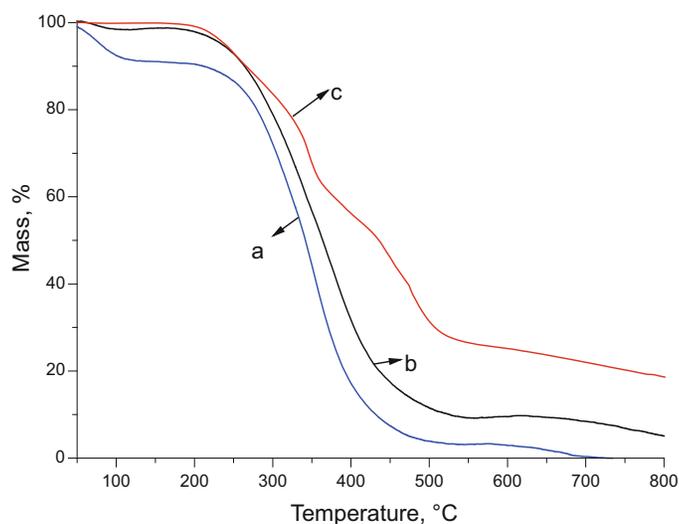


Fig. 3 TGA curves of furfural extract oil (a), thermally condensed oil (b) and COPNA resin (c)

of COPNA resin. After heat treatment, the polymerization degree has increased and side-chain cleavage occurred and the content of heavy aromatics has increased remarkably. COPNA resin has been successfully prepared from thermally condensed oil with PXG as a cross-linking agent and PTS as catalyst. In order to get a clearer understanding of the condensation and polymerization mechanisms, the average molecular structures of raw material and COPNA resin are obtained based on the results of FTIR, $^1\text{H-NMR}$, element analysis and average molecular weight analysis. The degree of polymerization is found to be around 3. The resulting COPNA resin with high heat resistance is a potential binder in carbon material preparation.

Nomenclatures

C_T	Total average carbon number
H_T	Total average hydrogen number
f_A	Ratio of aromatic carbon number to total carbon number
H_{AU}/C_A	Average condensation degree
σ	Hydrogen replaced rate surrounding aromatic rings of average molecular
R_T	Total average rings
R_A	Average aromatic rings
R_N	Average naphthenic rings
C_R	Average carbon number on the rings

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