SYNTHESIS OF CRUDE OIL POUR POINT DEPRESSANTS VIA POLYCONDENSATION OF CASHEW NUT SHELL LIQUIDS

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Summary

The polycondensation of cashew nut shell liquid (CNSL) with formaldehyde was carried out in order to synthesise a pour point depressant (PPD) for paraffinic crude oils. Experimental results showed that the obtained CNSL-formaldehyde novolac resin gave good performance, decreasing the pour point of crude oil by as much as 15°C. In addition, it was also showed that there is an optimum molecular weight value of the synthesised polymer, with which the ability for depression of pour point of crude oil is expected as maximum. Thus, it is believed that with proper molecular weight control, CNSL could be polymerised into a good PPD for local crude oil.

Key words: *Pour point depressant, paraffinic crude oil, cashew nut shell liquid, polycondensation, novolac resin.*

1. Introduction

With a high content of paraffin, c.a. 17 - 30wt%, of which 50% or more are high (solid) paraffin, Vietnamese crude oil is classified as paraffinic crude oil and has a high pour point, typically in the range of 27 - 38°C. This high pour point may cause some serious problems in production, transportation, and storage; and pose the need for use of an effective pour point depressant (PPD) additive. In general, a PPD is a high molecular weight substance that may effectively disperse and hinder the growth of oil's paraffin crystals when adsorbing on them. Ideally, the structure of PPD consists of (i) a paraffin-like part, which can co-crystallise with paraffin components of crude oil; and (ii) a polar part, which limits the level of co-crystallisation [1, 2]. Copolymers of alkyl acrylates and maleic anhydride are common PPDs used in practice [3 - 5].

Cashew nut shell liquid (CNSL) is a cheap, renewable and abundantly available raw material in Vietnam as it is a by-product of the cashew industry. The chemical composition analysis of typical CNSL [6] (Table 1) shows that it contains a major part of anacardic acid and cardol, which can act as reagents for a variety of reactions for the manufacture of a large number of products, including inhibitors, detergents, dispersants, and EP additives [7].

Table 1. *Typical chemical composition of CNSL*

Component	Content in CNSL (%)
Cardanol (%)	1.20
Cardol (%)	11.32
2-methyl cardol (%)	2.04
Polymer (%)	20.30
Anacardic acid	64.93

It is widely accepted that anacardic acid with proper thermal treatment yields four types of cardanols, which almost have the ready-made chemical structure of an additive. The chemical structures of cardanols found in CNSL are shown in Fig.1 [8]. It is observed that the C15 linear side chains of cardanols offer excellent solubility in

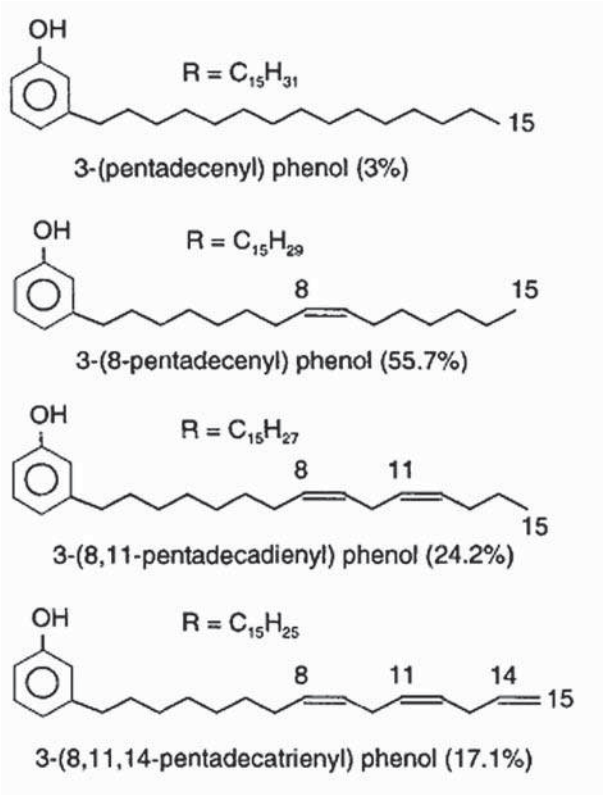


Fig.1. *Cardanols obtained from distillation of anarcadic acids in CNSL*

diesel oils and light lubricating oils, and the strongly polar phenol group will induce anti-oxidant characteristics.

The cardanols in CNSL can react with formaldehyde, in the presence of an acidic catalyst, to form a novolac type resin, which has the typical chemical structure as described in Fig.2. Having an ability to disperse paraffin molecules [7], these resins could be good PPDs for paraffinic crude oil. The synthesis of novolac type resin from cardanol and formaldehyde is well documented in relevant literatures [9, 10]. Starting from CNSL, after thermal treatment to convert anacardic acids to cardanols, ideally, a vacuum distillation step is carried out to produce pure cardanol for use in polycondensation reactions. However, this makes the whole process more complex and costly in terms of technology and energy demand. Therefore, in our study, novolac type resins are prepared directly from thermally treated CNSL. This paper presents the preliminary results of our research on polycondensation reactions, and the performances of the obtained products on the depressions of Vietnamese (paraffinic) crude oil's pour point.

2. Experiment

2.1. Synthesis of CNSL- formaldehyde novolac resin

CNSL was first decarboxylated by heating in order to convert most of its anarcadic acid component to cardanol. The decarboxylated CNSL (*deca-CNSL*) was then directly used as starting material in the synthesis of novolac type resin described below. The results of acidic value analysis show that the content of cardanol in the obtained deca-CNSL is 79.3 - 80.2wt%.

Novolac resins were prepared from deca-CNSL and formaldehyde with oxalic acid as catalyst, with the cardanol to formaldehyde molar ratio varying from 1:0.4 to 1:0.95. The amount of oxalic acid catalyst used was 0.25mol% based on the amount of cardanol. Polycondensation was carried out in dimethylformamide (DMF) solvent. Typically, 63g deca-CNSL, a pre-calculated amount of paraformaldehyde, 0.05g of methyl hydroquinone (MEHQ) and 0.5g oxalic acid were fed into a 500ml four-necked flask fitted with contact thermometer, stirrer, dropping funnel and water separator. With stirring and nitrogen blanketing, the reaction mixture was heated to 120°C. Samples were taken after 90 min. of reaction time for viscosity measurement in order to evaluate the progress of polymerisation.

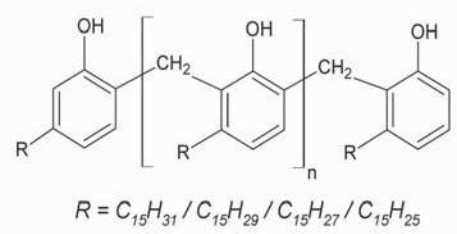


Fig.2. *Typical chemical structure of CNSL-formaldehyde novolac resin*

2.2. Analysis of products

Ubbelohde capillary viscometer (SYD-265B Petroleum Products Kinematic Viscosity Tester) was used for viscosity measurement at 40°C.

CNSL-based polymers were analysed by GPC (Agilent 1100 GPC) to determine the average molecular weights of starting materials and the polymer products obtained. Mic A separation column with capillary size of 5×10^2 - 10^5A° was used for measurement at 30°C.

FTIR (Bruker-EquinoX55) measurement was carried out for polymer products to confirm the structure of novolac resin. Samples were applied as thin layers on KBr pellets, and scans were performed in the wavenumber range of 4,000 - 400cm^{-1}.

2.3. Determination of pour point of FO and FO/PPD mixtures

The *deca-CNSLs* and polymers were used for decreasing pour point of Su Tu Den crude oil, which contains 23.6% n-paraffin of C_{10} - C_{40} [11], and has a measured pour-point of 27°C. Each PPD product was mixed with various solvents to form 50wt% PPD solutions. The PPD solution was then mixed with crude oil to reach the final content of PPD in the mixture of 0.5wt%. After that, pour points of the mixtures were determined in accordance with ASTM D97. "Blank PPD solution" containing only solvent was also prepared and tested in order to exclude the pour point decreasing effect of pure solvent.

3. Results and discussion

3.1. Decarboxylation of CNSL

Basically, the decarboxylation process leads to a decrease in acidic value of CNSL. Two parameters affecting this process are temperatures and treating times. Fig.3 presents changes of acidic value of CNSL at different temperatures and treating times. It is clear to see that 160°C and 60 mins are the most appropriate temperature and treating time, respectively. Another important point is that the treating time should not exceed 60 mins, since the prolonged thermal treatment will induce polymerisation

of CNSL. Fig.4 shows the variation of viscosity of CNSL with temperatures at different durations of treatment. As the decarboxylation proceeds, the viscosity of CNSL gradually declines due to lower viscosity of cardanol compared to that of anarcadic acid [12]. However, after about 60 mins, a slight increase of viscosities could be observed at all temperatures.

3.2. Synthesis of CNSL-formaldehyde novolac resin

As for the polycondensation of deca-CNSL to form novolac type resin, it was observed during the experiment that the reaction was exothermic, with relatively fast increase in viscosity of the product. Even though methyl hydroquinone was used to prevent self-polymerisation of unsaturated alkyl side chains of CNSL, the viscosity of the reaction mixture was found to hugely increase after 2 hours of reaction time, which was calculated after the addition of the final drop of formaldehyde. This seems to suggest that the polymerisation of CNSL side chains is inevitable as the polycondensation is prolonged at high temperature. Since it was aimed to determine the effect of the polycondensation product in decreasing the pour point of crude oil, only the sample products obtained before 2 hours of reaction were further used for pour point measurements.

FTIR spectrums of deca-CNSL and the product obtained by polycondensation are shown in Fig.5. It can be observed from Fig.5 that new characteristic peaks appear at wavenumbers 1,640cm^{-1} and 1,614cm^{-1}; and the shift and deformation of peak at 1,076cm^{-1} (for deca-CNSL) to 1,094cm^{-1} (for the product) which are due to the C=O stretching from methylol groups. At the same time, the peaks at 3,010cm^{-1}, 1,590cm^{-1} and 778cm^{-1} all remain unaffected. All these facts are identical with those given in previous studies [13] and indicate that the polymerisation has occurred via substitution of methylol groups rather than through the double bonds of the side chains.

During the polycondensation, with increasing content of paraformaldehyde, the viscosity of the reaction mixtures was found to increase (Fig.6), which means the molecular weight of obtained novolac resins increases. GPC measurement results reveal that molecular weights increase from 350g/mol to 9,000g/mol and 25,000g/mol, for the reaction mixtures with the CNSL/paraformaldehyde ratio of 1:0.4 and 1:0.9, respectively. The significance of these results is that the molecular weight of the novolac resin product could be effectively controllable with varying ratios of the reactants.

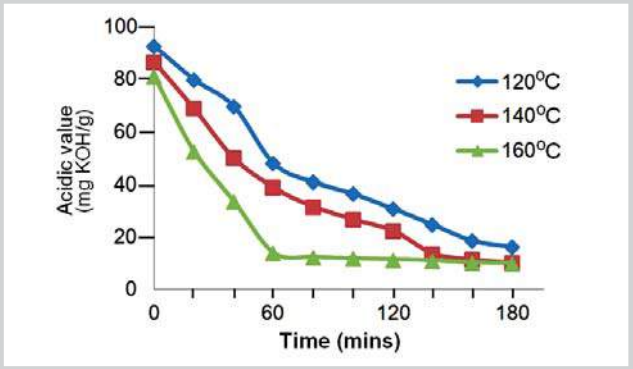


Fig.3. *Variation of acidic value of CNSL with temperatures and time of decarboxylation process*

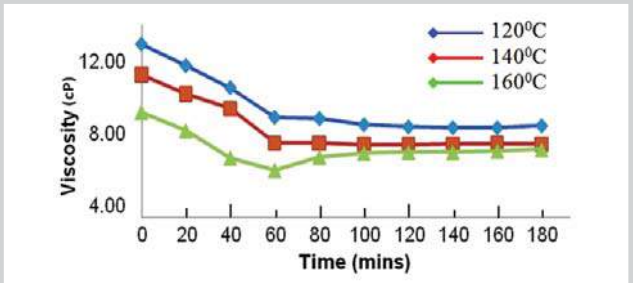


Fig.4. *Variation of viscosity of CNSL with temperatures and time of decarboxylation process*

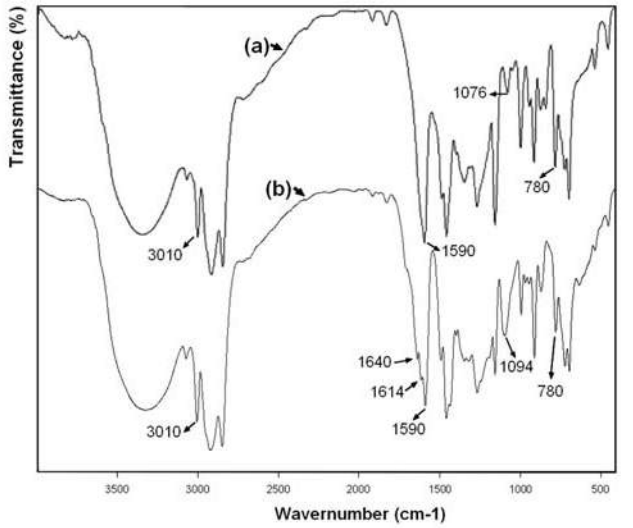


Fig.5. *FTIR spectrums of (a) deca-CNSL and (b) novolac resin product*

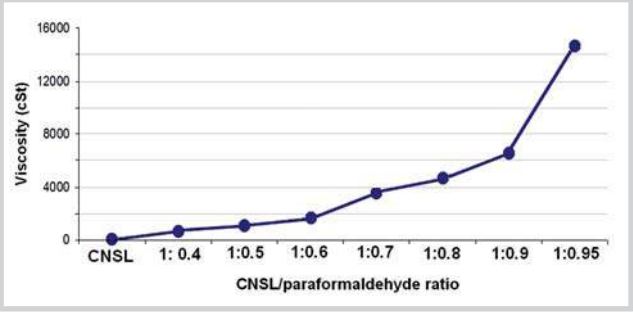


Fig.6. *Viscosity of reaction mixture at different CNSL/paraformaldehyde ratios*

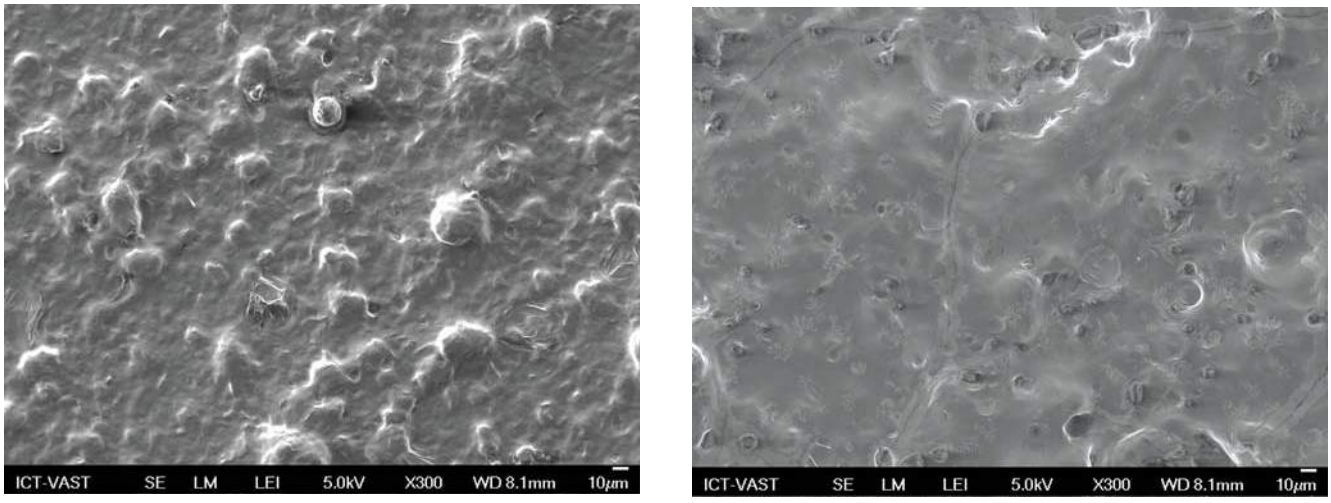
3.3. Pour point depressing ability of CNSL - formaldehyde novolac resins

As the direct dissolution of the resin into crude oils is proved to be a difficult process due to poor solubility and high viscosity of the crude oil, CNSL-formaldehyde novolac resins were first dissolved in a specific solvent prior to mixing with the crude oil. The choice of proper solvent is of great importance. A polar solvent (DMF) and a non-polar solvent (xylene) were tested for the dissolution of novolac resins. Table 2 presents the pour point depression capability of different dissolved resins for Su Tu Den crude oil. It could be seen that DMF dissolved resins show significantly better performance compared to xylene dissolved ones. When 0.5% DMF dissolved resin is added to Su Tu Den crude oil, the pour point could drop by 12 - 15°C, whereas a decrease of only 3 - 6°C in pour point of crude oil was observed for xylene dissolved resins. It is also important to notice that the solvents themselves, despite their low freezing points, do not have any pour point depressing ability, as the blank samples have the same pour points as the crude oil. This could be explained by the fact that solvent molecules, with much more smaller size compared to crude oil molecules, could not prevent the crystallisation and growth of large crystalline of paraffin molecules of the crude oil. Also, the small size molecules cannot induce any spatial arrangement to separate paraffin crystalline or to prevent the formation of a paraffin crystalline network in crude oil.

In our previous study, SEM observations of the crystallised surfaces of crude oil/PPD mixtures were carried out and shown in Fig.7 [16]. The surface of crude oil without PPD (Fig.7a) is covered with large paraffin crystals, while in the case of crude oil with PPD (Fig.7b), paraffin molecules seem to be unable to form a network and hardly crystallise, resulting in a smaller size and lower numbers of crystals. This could be attributed to the ability of the PPD novolac resin molecules in adsorbing on and then dispersing the paraffin microcrystallines in the crude oil. Linear alkyl chains of the resins ("R" in Fig. 2) could adsorb on the surface of paraffin microcrystalline, while bulky phenolic groups, connected via methylene bridges, could well separate the microcrystallines apart. As the result, the fluidity of crude oil/PPD mixture is maintained, at much lower temperature, compared to the neat crude oil.

Table 2. *Pour point depression ability of different dissolved resins, mixed to Su Tu Den crude oil at 0.5wt%*

Solvent	Type of resins	Pour point (°C)	Solvent	Type of resins	Pour point (°C)
DMF	No resin	27	Xylene	No resin	27
	1:0.4 resin	15		1:0.4 resin	24
	1:0.5 resin	15		1:0.5 resin	24
	1:0.6 resin	12		1:0.6 resin	24
	1:0.7 resin	12		1:0.7 resin	24
	1:0.8 resin	12		1:0.8 resin	21
	1:0.9 resin	12		1:0.9 resin	21



(a) *(b)*

Fig.7. *SEM photographs of surface of (a) freezed neat crude oil and (b) freezed crude oil/CNSL-novolac resin*

4. Conclusions

Polycondensation of CNSL with paraformaldehyde, forming novolac resin, seems to be a promising method in production of pour point depressants. CNSL-formaldehyde novolac resins, with a content of 0.5wt%, could reduce the pour point of paraffinic crude oil by 12 - 15°C. It is also worth noticing that the pour point depressing capability of a resin is a function of its molecular weight. This makes the tailoring of resin's molecular weight an effective measure to obtain a PPD of desired ability. Furthermore, the significance of solvent employed to dissolve PPD prior to mixing with crude oil could not be neglected, and further investigations will be carried out to clarify the role of solvent and the mechanism that governs the depression of pour point of the crude oil.

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