DOI 10.1007/s10553-023-01512-w
Chemistry and Technology of Fuels and Oils, Vol. 59, No.1, March, 2023 (Russian Original No.1, January–February, 2023)

INNOVATIVE TECHNOLOGIES OF OIL AND GAS

LOW-TEMPERATURE FLOW PERFORMANCE IMPROVER FOR SADDLE DIESEL

Lingli He, Xiaozhu Long ✉

Saddle Diesel is a diesel engine plant in a local city in northeast China, which is already the special designation. In this paper, a new polyhydroxy polyacid macromolecule called citric acid-1,4-butanediol-citric acid-cycloalkanic acid-tetradecyl alcohol (CTC-NT) with 1,4-butanediol as the core was designed and synthesized via an "ester-ester" copolymerization process using 1,4-butanediol and citric acid as the raw materials and then grafted sequentially with naphthenic acid and tetradecanol containing functionalized groups. The structures of the synthesized compounds were characterized by nuclear magnetic resonance and infrared spectroscopy, and the results showed that the synthetic products were consistent with the designed molecular structure. The use of the prepared CTC-NT in saddle oil light diesel was studied. The results showed that the filtration improvements of the synthesized multibranched macromolecule CTC-NT were better than those of other additives for the same oil, and the cold filter point was reduced by up to 13°C when the dosage was 900 μg/g.

Keywords: multibranched macromolecules, spatial structures, pour point depressant, saddle diesel, cold filter plugging point – CFPP.

Diesel filters are blocked at low temperatures due to the formation of spatial structures caused by facile precipitation of wax crystals leading to wax deposition. Diesel fuel low-temperature flow performance improver (DFI) is a functional macromolecular oil-soluble polymer that changes the wax morphology in diesel and improves the diesel low-temperature flow performance [1] by reducing wax crystal aggregation and bonding. The crystalline state of paraffin in the diesel fuel can generally be altered by solubilization, adsorption, nucleation, and cocrystallization [2, 3]. The DFI prepared in the current research mainly comprises comb polymers with long multibranched alkyl chains, such as those seen in ethylene-vinyl formate copolymers [4, 5], acrylate polymers, ethylene-vinyl acetate copolymers (EVA), etc. The addition of the DFI not only reduced the CFPP, but also improved the cold flow performance of the diesel fuel, as well as the diesel output and economic benefit. Therefore, it is of scientific and practical significance to prepare a diesel low-temperature flow improver with an excellent filtration reduction effect. This paper is designed to produce a new low-temperature diesel flow addition, which was studied and prepared by the Anshan refinery of Liaoyang Petrochemical Company using light diesel produced from imported mixed crude oil. The type of diesel that was selected

College of Chemical Engineering, Shenyang Institute of Chemical Technology, Shenyang, Liaoning, China. *Corresponding author: Xiaozhu Long* ✉. *E-mail: longxiaozhu10@163.com.* Translated from *Khimiya i Tekhnologiya Topliv i Masel*, No. 1, pp. 108–112 January–February, 2023.

is 10#. Considering the use of diesel in low temperature environment, this type of diesel can be used at -5°C, which basically meets the use conditions of diesel in most areas of China in winter.

1. Experimental

Raw materials and instruments. Tetradecanol, citric acid, and 1,4-butanediol were chemically pure and were obtained from Sinopharm Shanghai Chemical Reagent Co., Ltd.; Petroleum ether (60-90°C) was chemically pure and was obtained from Shenyang Far East Reagent Factory, China; Triphenylphosphine, chloroform, absolute ethanol, toluene, acetone, dimethyl sulfoxide, and benzene were analytically pure and obtained from Shenyang Far East Reagent Factory, China; Ethyl acetate were chemically pure and were obtained from Tianjin Bodi Chemical Co., Ltd, China; Home-made alcohol-aqueous solutions were prepared by mixing 1 volume of deionized water and 2 volumes of absolute ethanol. Industrial grade naphthenic acid was a dark brown oily liquid obtained from Sigma Aldrich (Shanghai) Trading Co., Ltd. , China; its acid value was approximately 230 mg KOH/g. Sample crude oil: -10# light diesel was obtained from the Liaoyang Petrochemical Company Anshan Refinery, and commercially available -10# light diesel was obtained from the PetroChina Gas Station Desheng Store, China.

A Nicolet Model iS50 Infrared Absorption Spectrometer was obtained from Thermo Fisher Scientific, China, a ^{1}HNMR instrument (Bruker 500 MHz) and a TMS internal standard from Brooke Scientific Instruments, Hong Kong Co., Ltd. were used for the NMR studies, and a DDW-A multifunctional cryometer was obtained from Shenyang Shiboda Instrument Co., Ltd, China.

Synthesis of CTC-NT macromolecules. 1,4-Butanediol, citric acid, triphenylphosphine, and toluene were added to a 250 ml three-mouth flask and heated and stirred in an oil bath. The temperature of the reaction was controlled within 115-130°C until the effluent reached a certain amount (theoretical effluent value); heating was stopped, and the solution was stirred and evacuated (vacuum pressure: 0.06 MPa) for 35-65 minutes, the triphenylphosphine, toluene and some unreacted citric acid were separated, and a yellowish solid was obtained. After cooling to 80°C, crude naphthenic acid, toluene, and triphenylphosphine were sequentially added to a 250 ml three-mouth flask and heated to 120°C in an oil bath with mechanical stirring. When the amount of effluent in the water trap exceeded the theoretical amount of effluent, heating was paused and the solution was stirred as it cooled to below 100°C. Finally, tetradecanol was added, and the reaction was continued until the amount of effluent exceeded the theoretical value. Then, the reaction was stopped and considered to have reached completion. The crude citric acid-1,4-butanediol-citric acid-naphthenol-tetradecanol (CTC-NT) was obtained as a dark yellow product after evacuation (vacuum pressure: 0.06 MPa) at 160-170°C for 35-65 min.

The obtained CTC-NT solid was added to a dustless beaker, immersed in an 80°C “alcohol-water” mixed solution, and stirred mechanically for 5 min. The mixture was poured into a separatory funnel, allowed to stand, and the alcohol-water solution was removed after layering; this sequence was repeated 5 times. Then, the solvent and catalyst were washed. To remove the ethanol, the refined yellow–brown CTC-NT was obtained by washing with deionized water at 60 °C three times, followed by drying in an oven at 85°C for 8 hours.

The synthetic route to compound CTC-NT was as follows: “citric acid-1,4-butanediol-citric acid” polyhydroxy polyacid was synthesized via esterification of 1,4-butanediol with citric acid , and then the target product was synthesized by partial esterification with naphthenic acid and moderate esterification with tetradecanol. After the synthetic product was partially esterified with naphthenic acid, the steric hindrance was limited [6], its effects on the subsequent reactions were not large, and the yields were high. The synthetic route is shown in **Figure 1**.

Structural characterization and performance tests. The CTC-NT samples were studied by FTIR using the potassium bromide pellet method and a wavenumber range of 4000 to 450 $cm^{-1}$and^{1}H NMR spectra were obtained at a working frequency of 500 MHz on samples dissolved in $CDCl_3$ solvent. According to the NB/SH/T 0248-2019 standard method, the difference between CFPP added with filter reducer diesel and CFPP added with blank diesel (ΔCFPP) was used as the index to evaluate the filter reduction effect of the modifier. The target product was added to various solvents to observe the dissolution behaviors to complete the solubility test.

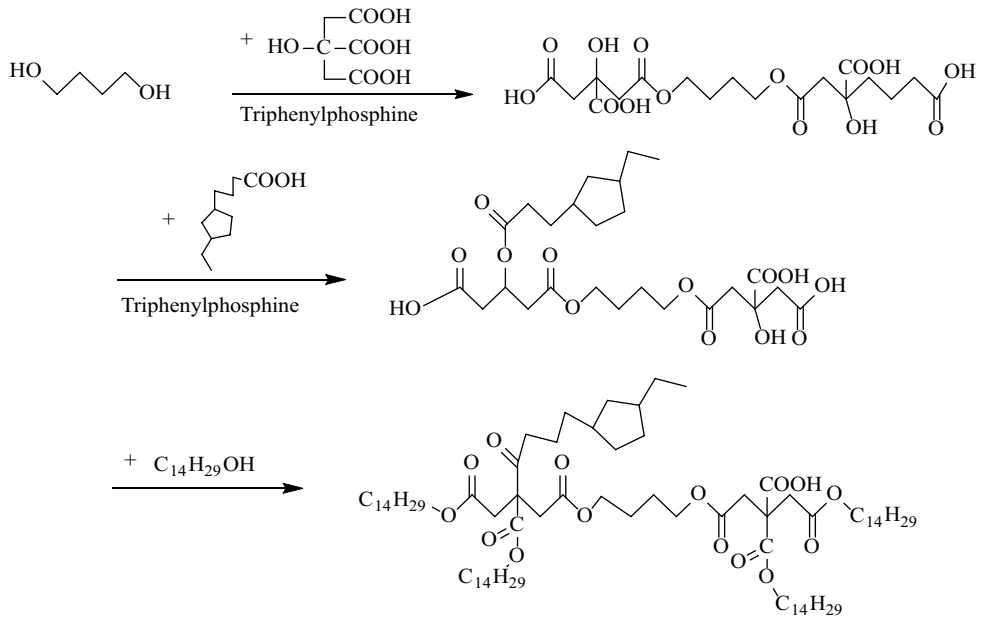

Fig. 1. Synthetic roadmap to CTC-NT

2. Results and discussion

In the infrared spectra shown in **Fig. 2**, the strong absorption peaks of interest for the CTC-NT appeared at 1464 cm^{-1}, 2854 cm^{-1}, 2922 cm^{-1}, and 1189 cm^{-1}, indicating that there were hydroxy-OH peaks in the molecule; there were strong absorption peaks at 1464 cm^{-1}, 2922 cm^{-1}, 2954 cm^{-1}, and a moderate absorption peak at 723 cm^{-1}, indicating (CH_2)n-methylenes in the molecule; and a strong absorption peak at 1738 cm^{-1} and a strong absorption peak at 1189 cm^{-1}, indicating the presence of ester-COOR groups in the molecule. The functional groups of the resulting product were as expected for the desired product.

$CDCl_3$ was used to obtain ^{1}HNMR spectra for CTC-NT .In the ^{1}HNMR spectrum shown in **Fig. 3**, the prepared CTC-NT showed strong peaks from 4.0496 to 4.2127 for the Hs of methylene groups (O–CH_2) linked to oxygen. The high-field peaks appearing at 2.2812-2.3514 belonged to hydroxyls (OH) connected to tertiary carbon atoms and Hs in methylenes (CH_2) connected to carbonyl groups (CH_2–C=O) [7], and the peaks appearing at 1.6018~1.7312 were for Hs in the naphthyl group and (CH_2–OCO–CH_2); the high-field peaks at 1.2556, 1.2969 and 1.3091 arose from methylenes $(CH_2)_n$–H in the long carbon chains; the high-field peaks contained three independent peaks at 0.8685, 0.8801 and 0.8912 ppm, respectively, which belonged to Hs in the methyls (CH_3) connected to long-chain end-groups. As a result, the multibranched macromolecules synthesized were consistent with the designed product.

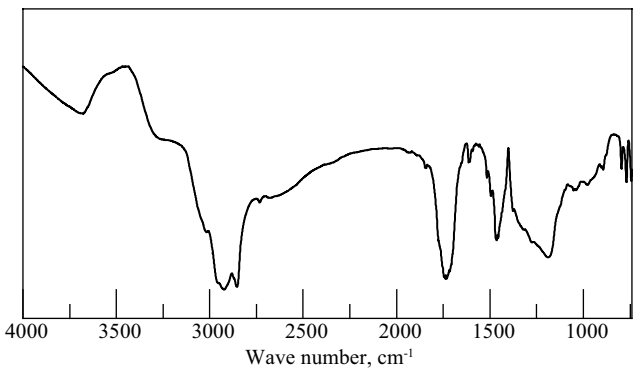

Fig. 2. Infrared spectrum of the target product CTC-NT

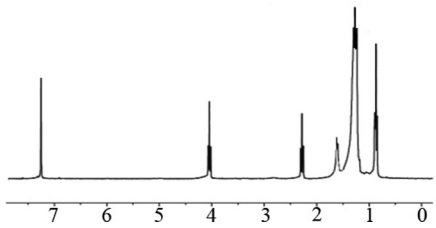

Fig. 3. ^{1}H NMR spectrum for the prepared CTC-NT

Table 1. Solubilities of CTC-NT

Solvents	Solubilitiy
Water	not dissolved
Ethanol	dissolved
Dimethyl sulfoxide	dissolved
Ethyl acetate	dissolved
Acetone	dissolved
Benzene	dissolved
Chloroform	dissolved

Table 2. Effects of Different CTC-NT Doses on Filtration

Dose (μg/g)	ΔCFPP (°C)
600	6
700	8
800	10
900	13
1000	9
1100	7

Table 3. Filtration Aid Effects of CTC-NT with Different Oils

Oil	ΔCFPP (°C)
Oil refinery -10# diesel	13
Homemade -10# diesel	10
Commercial -10# diesel	8

The experimental results are presented in **Table 1**. Solubility tests were carried out with the product, and a variety of solvents were added to the target product to observe dissolution. Because the CTC-NT molecule contained polar ester groups, hydroxyl groups and carbonyl groups, its behavior was similar to those of the polar groups in ethyl acetate, ethanol, acetone, and dimethyl sulfoxide. Weakly polar alkyl groups show similar interaction forces with chloroform, benzene, etc. Therefore, CTC-NT was insoluble in water but soluble in organic solvents such as ethanol, dimethyl sulfoxide, ethyl acetate, acetone, benzene, and chloroform.

The filtering performance data for the prepared CTC-NT multibranched macromolecules are shown in **Tables 2, 3**, where ΔCFPP (the reduction value of the cold filter plugging point) is the difference (°C) between the CFPP of the diesel fuel with a filter reducer added and the CFPP of untreated diesel fuel. ΔCFPP reflects the ability of the newly synthesized CTC-NT macromolecular additive to improve the cold flow performance of diesel fuel. The experimental results are shown in Table 2, and the best results were obtained when the additive was dosed at 900 μg/g. The same cold filtration point test method was used to compare the filtration aid properties of different oils, and the data in Table 3 show that CTC-NT had better filtration reduction ability and good compatibility with -10# diesel oil produced from crude oil used in the Anshan refinery and filtration aid capability for homemade and commercially available -10# diesel oils.

3. Conclusion

In this paper, 1,4-butanediol, citric acid, naphthenic acid and tetradecanol were selected as raw materials, and triphenylphosphine was used as a catalyst for -10# light diesel produced from the crude oil of the Anshan refinery of the Liaoyang Petrochemical Company. The oil-soluble polymeric macromolecule citric acid-1,4-butanediol-citric acid-naphthenic acid-tetradecanol (CTC-

NT) was successfully developed as a low-temperature fluidity improver. The results of IR and ^{1}HNMR studies of the synthesized products showed that the CTC-NT multibranched macromolecule was synthesized and the structure was consistent with the designed molecular structure. CTC-NT is a yellow–brown solid that is insoluble in water and soluble in ethanol, dimethyl sulfoxide, ethyl acetate, acetone, benzene, chloroform and other organic solvents. For a dose of 900 μg/g, the cold filtration point of light diesel fuel was reduced by up to 13°C with the synthesized CTC-NT.

Acknowledgements

National Natural Science Foundation of China (61403263).

REFERENCES

1. M. Madani, M. Keshavarz Moraveji and M. Sharifi, "Modeling apparent viscosity of waxy crude oils doped with polymeric wax inhibitors," *J. Pet. Sci. Eng.*, **196**, 108076 (2021).

2. X. Z. Long, C. S. Wang, Z. Y. Ma, Y. W. Tian and X. Li, "Synthesis and characterization of a new claw molecule as diesel low-temperature flow improver," *Pet. Sci. Technol.*, **27**, 1592-1603 (2009).

3. C. H. Xiong, G. Y. Tian and L. L. Ren, "The correlation of physico-chemical properties with hydrocarbon groups of diesel," *Acta Pet. Sin.*, **26**, 551 (2010).

4. L. Sun, X. Lu, Q. Bai and Z. Wang, "Triple-shape memory materials based on cross-linked ethylene-acrylic acid copolymer and ethylene-vinyl acetate copolymer," *Polym. Eng. Sci.*, **62**, 2692-2703 (2022).

5. P. Gu and J. Zhang, "Vinyl acetate content influence on thermal, nonisothermal crystallization, and optical characteristics of ethylene–vinyl acetate copolymers," *Iran. Polym. J.*, **31**, 905-917 (2022).

6. X. Z. Long, C. S. Wang, Y. W. Tian and Z. Y. Ma, "Synthesis, characterization and application of claw macromolecules of citric acid 1,4-butanediol-citric acid-stearic acid-stearyl alcohol," *Polym. Mater. Sci. Eng.*, **25**, 24-27 (2009).

7. A. Deckers, B. Wenderoth, T. Rühl, H. J. Müller and R. Klimesch, Ethylene-vinyl formate copolymers, process for their preparation, their use as flow improvers, and fuel and propellant compositions comprising them, US Patent, 6235069, 2001-05-22.