Structure Characterization and Solubility Analysis of the Existent Gum of the Fischer–Tropsch Synthetic Crude

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ABSTRACT: The existent gum content of the Fisher–Tropsch synthetic crude exceeded the standard seriously, affecting its transportation and use. To determine the structure of the existent gum extracted from the Fisher–Tropsch synthetic crude, elemental analysis, Fourier transform infrared (FT-IR) spectroscopy, nuclear magnetic resonance (NMR), and X-ray photoelectron spectroscopy (XPS) were employed to determine the chemical structure of the gum. The Brown–Ladner method is used to calculate the average structural parameters and the average molecular formula of the existent gum. The results show that the existent gum of the Fisher–Tropsch synthetic crude is composed of heterocyclic aromatic hydrocarbons and short-carbon paraffins. Compared with petroleum gums and coal tar gums, the existent gum content of the Fisher–Tropsch synthetic crude has the characteristics of high aromaticity, short side chains, and nitrogen-containing heterocycles. After being oxidized, its aromaticity further increases, more closed loops are formed, and the side chain is further shortened. This is caused by a complex oxidation reaction during the oxidation process. Molecular dynamics simulation calculations were performed to reveal the T-stacked morphology of the existent gum of the Fisher–Tropsch synthetic crude in a mixed solvent of acetone and toluene.

1. INTRODUCTION

During the storage of fuel oil products, certain types of hydrocarbons in the fuel mixture can slowly react with oxygen in the air at ambient temperature. The oxidation products produced by these oxidation reactions form an insoluble solid, commonly referred to as sediment or gum. The accumulation of these substances can cause engine wear and adversely affect engine efficiency, performance, emissions, and durability.1–3 Gum plays a vital role in maintaining the stability of fuel oil products. It directly affects the accumulation of asphaltenes in the dynamic gum in the system through adsorption on the asphaltene surface and the formation of a stable space alkyl chain layer to maintain the stability of the entire gum system.14–8 The existent gum content in oil products is an important indicator of oil product evaluation. It has an important influence on the quality of gasoline and diesel products. Therefore, the research on gum is of great significance.

Li et al.3 discovered that Liaohe gum consists of anthracene, two cycloalkanes, and six alkyl chains grafted on the ring structure core. Zhang et al.9 analyzed the composition and structure of gums in crude oil from the South China Sea and pointed out that it is a molecule with an aromatic ring connected by an alkyl chain. Grinstein et al.10 found that the average molecular weight of USA heavy oil gum is between 558 and 845 through fractionation and pointed out that this kind of gum molecular paraffin chain has a small length and a slightly branched block structure. Collell et al.11 analysis showed that the average molecular formula of gum in American shale oil is C_{33}H_{32}O, which is composed of condensed aromatic rings with alkyl side chains and several naphthenic rings. Yang et al.12 used 1H NMR/IR method to calculate the average molecular structure parameters of Fengcheng heavy oil gums and speculated that the molecular model of Fengcheng heavy oil gums contains more aromatic carbons and chain alkyl carbons. Power et al.14 compared the spectra of soluble gums and insoluble gums formed during accelerated aging and environmental aging of fuels by infrared spectroscopy of products related to the instability of petroleum diesel distillates, and pointed out that the gum in the accelerated aging fuel is different from the gum formed during environmental storage. Hazlett et al.15 used pyrolysis field ionization mass spectrometry to analyze diesel solids under several different aging conditions in detail and found that the filterable gums and the attached gums have similar components, but the filterable solids which come from different fuels were significantly different. Kawahara et al.16 pointed out alkoxy groups are produced by hydroperoxides, peroxyxides, and alkyl peroxy radicals. Pereira et al.17 studied the effects of adding...
different amounts of absolute ethanol and copper to the formation of gums in Brazilian gasoline and found that adding absolute ethanol to gasoline is not conducive to the formation of gums in gasoline, and pointed out that the presence of copper will accelerate the formation of gum. Pedley et al.\textsuperscript{18} found that nonbasic nitrogen compounds, especially alkyl indoles, were important components of fuel deposits through the study of diesel stability.

Frankenfeld et al.\textsuperscript{19} used pure nitrogen compounds in the petroleum simulated fuel system to study the effects of nitrogen-containing compounds on sediment formation and found that the presence of nitrogen-containing compounds promoted sediment formation. Mushrush et al.\textsuperscript{20} found that short-chain multisubstituted pyrrole exposed to air is likely to form hydrogen peroxide compounds and may provide free radicals for other oxidation peroxides. Correa et al.\textsuperscript{21} pointed out that free radicals are very sensitive to fuel matrix and chemical environment. Doyle et al.\textsuperscript{22} reported the oxidation of alkyl radicals, pointing out that alkyl peroxy radicals can be used to further react to form more complex molecules.

At present, the replacement of conventional hydrazine fuels with highly efficient and low-toxic liquid oxygen + kerosene is the development trend of the world’s space propulsion technology. At present, China is developing a coal-based aerospace kerosene, and the raw material, the "GB/T 8019-2008 standard test method for gum content in fuels by jet evaporation" was adopted to determine the content of the raw material oil and the oxidized oil in the existent gum. The procedure was as follows: after washing the beaker with gum molecule solvent until there was no gum, the beaker was washed with ultrapure water several times, clamped with stainless steel pliers and placed in a 150 °C drying oven for 1 h, then taken out, and placed in a desiccator to cool. The exact 25 mL of oil was measured by a pipette and poured into the beaker. And then, the beaker was held by the pliers into the groove of the metal bath heated to 180 ± 3 °C and the oil-free air compressor was turned on. The initial flow rate indicated by the flow meter is 20 ± 2 L·min\textsuperscript{-1}. Within the first 20 min, the flow rate was gradually increased to 55 ± 5 L·min\textsuperscript{-1}. When the oil and gas stopped flowing and the beaker bottom and beaker wall showed dry residues or oily residues that no longer decreased, the evacuation was considered to be complete. After the evacuation was complete, the beaker was placed in a desiccator and cooled for 30–40 min before weighing. The treatment of the beaker with gum was repeated until the difference between successive weighing did not exceed 0.0004 g. At this time, the residual substance inside the beaker was the existent gum. After the measurement, the content of the raw oil and oxidized oil in the existent gum were 12.2/100 and 21.6/100 mg, respectively.

Oxidized oil was prepared according to "SH/T 0175-2004 Distillate Fuel Oil Oxidation Stability Determination Method (Accelerated Method)".\textsuperscript{32} The process is as follows: first, fill the oxidation tube with water containing cleaning agent, install the oxygen tube and condenser, soak for at least 2 h, scrub, pour out the washing liquid, rinse with tap water five times, then rinse with distilled water three times, wash with acetone, remove water, and dry for use; then, filter the sample with a 0.45 μm filter membrane, take 350 ± 5 mL of the filtered sample into the oxidation tube, pass the oxygen at the rate of 50 ± 5 mL·min\textsuperscript{-1}, oxidize at 95 ± 0.2 °C for 16 ± 0.25 h, and

\textbf{2. EXPERIMENTAL SECTION}

\textbf{2.1. Basic Properties of Raw Oil.} The raw oil used in the experiment is the product oil provided by a factory in Ningxia, China. Its basic properties are shown in Table 1.

\begin{table}[h]
\centering
\caption{Main Properties of Feedstock for the F−T Synthetic Crude}
\begin{tabular}{lll}
\hline
\textbf{items} & \textbf{value} & \textbf{detection basis} \\
\hline
density (20 °C)/g·mL\textsuperscript{-1} & 0.7563 & GB/T 1885-1998 \textsuperscript{28} \\
viscosity (40 °C)/mm\textsuperscript{2}·s\textsuperscript{-1} & 1.439 & GB/T 265-1988 \textsuperscript{29} \\
acidity/mg KOH/(100 mL)\textsuperscript{-1} & 0.55 & GB/T 258-2016 \textsuperscript{30} \\
sulfur content/mg·L\textsuperscript{-1} & 0.23 & NR/SHT 0842-2017 \textsuperscript{31} \\
existen gum content/mg/(100 mL)\textsuperscript{-1} & 12.2 & GB/T 8019-2008 \textsuperscript{27} \\
metal content (ω)/(/μg·g\textsuperscript{-1}) & Fe/Ca 12.07/2.44 & Na/Mg 1.63/0.26 \\
\hline
\end{tabular}
\end{table}

\textbf{2.2. Gum Extraction.} Using the F−T synthetic crude as the raw material, the "GB/T 8019-2008 standard test method for gum content in fuels by jet evaporation" was adopted to determine the content of the raw material oil and the oxidized oil in the existent gum. To investigate the molecular structure of the gum components, the existent gum was separated by "GB/T 8019-2008 standard test method for gum content in fuels by jet evaporation"\textsuperscript{27} and characterized by elemental analysis, Fourier transform infrared (FT-IR), nuclear magnetic resonance (NMR), X-ray photoelectron spectroscopy (XPS), and other analytical methods. The average molecular structure number of the existent gum was calculated by the Brown–Ladner method. Finally, the aggregation morphology of the gum components in the mixed solvent was studied by molecular dynamics simulation. The study of the existent gum components of the F−T synthetic crude can provide the basic information for the optimization, transportation, and storage of its processing technology.
finally cool the oxidized sample to room temperature to obtain oxidized oil.

2.3. Characterization. 2.3.1. Elemental Analysis. The Elementar Vario Micro Cube element analyzer was used to analyze the C, H, S, and N element content in the existent gum molecule sample of the F−T synthetic crude. The sample was completely burned and decomposed under the high-temperature condition of 1150 °C, and the O element content is calculated by difference subtraction.

2.3.2. FT-IR Analysis. The Nicolet Magna 6700 Fourier transform infrared spectrometer was used for FT-IR analysis of the existent gum of the F−T synthetic crude. Test conditions were as follows: room temperature, the resolution of the instrument is 0.4 cm−1, infrared spectral scanning is carried out in the interval 400−4000 cm−1, the wavenumber accuracy is 0.01 cm−1, the cumulative scan is 32 times, and the potassium bromide is compressed for sample preparation (the mass ratio of gum to potassium bromide is 1:200).

2.3.3. Gel Permeation Chromatography (GPC) Analysis. The Agilent PL-GPC 220 high-temperature gel permeation chromatography was used to determine for average relative molecular weight (GPC) of the existent gum of the F−T synthetic crude. With tetrahydrofuran (THF) as the solvent, the flow rate was 0.6 mL·min−1, the injection volume was 10 μL, and the column temperature was 40 °C.

2.3.4. NMR Analysis. The Bruke Avance 400 nuclear magnetic resonance spectrometer was used to determine the 1H spectrum of the existent gum of the F−T synthetic crude. The resonance frequency is 125 MHz, 10 000 times total, delay time is 5 s, spectrum width is 31 000 Hz, the sampling time is 0.5 s, the relaxation reagent is deuterated chloroform (CDCl3), and the calibrator is tetramethylsilane (TMS).

2.3.5. XPS Analysis. The thermoelectric K-Alpha energy spectrometer was used to perform XPS energy spectrum analysis on the existent gum of the F−T synthetic crude. The excitation source is Mg Kα (energy is 1254 eV), the motion range is 100−4000 eV, the analysis chamber pressure is less than 5 × 10−9 Pa, the Al 2p (74.4 eV) spectrum peak is used as the internal standard, and the C 1s peak in the CC structure is used. The standard to eliminate the effects of charging effects is 284.8 eV. Thermo Avantage v 5.967 data analysis software was used for peak fitting.

2.4. Molecular Simulation. The molecular dynamics method was used to study the solvation of the gum molecules system, and the calculation and simulation processes were completed using Materials Studio software. The procedure was as follows: i) Solvent and solute molecules are constructed in Materials Studio, and the solvent and solute molecule models are optimized for energy minimization and geometric configuration under the COMPASS force field in the Forcite module, respectively; ii) The Construction unit in the Amorphous Cell module constructs a periodic solvent cubic box in which the solven and solute molecules are placed; iii) Kinetic annealing of the constructed periodic model is performed under Nose constant temperature hot bath; the calculation step is 1 fs; and the calculation time is 1500 ps.33,34

3. RESULTS AND DISCUSSION

3.1. Elemental Analysis and Relative Molecular Mass Analysis. Table 2 shows the average relative molecular mass and the content of each element of the existent gum of the F−T synthetic crude. The gum of the F−T raw oil (FRG) was 549, and the gum from the F−T oxidized oil (FOG) was 546. C8H14O3N0.86S can be used to express the average molecular formula of gum. The values of n, m, x, y, and z can be determined by the average molecular weight and the content of each element. The average formulas are C33.06H34.27O3.87N3.83S0.06 and C32.58H31.91O4.38N3.83S0.07, O/C ratios are 0.117 and 0.134, and H/C ratios are 1.036 and 0.979, respectively.

It can be seen from Table 2 that the petroleum and low-temperature coal tar gums have a low N content, both below 2%, an O content of about 6−7%, and their hydrogen−carbon ratios are all greater than 1.2. In contrast, the existent gum of the F−T synthetic crude has a very high heteroatom content, and the total content of O and N exceeds 20%, which is much larger than that of petroleum and low-temperature coal tar, and its hydrogen−carbon ratio is smaller. According to elemental analysis and relative molecular mass, it can be seen that the unsaturated functional groups such as aromatic rings and double bonds in the F−T synthetic crude gum account for a larger proportion.

In addition, from Table 2, it can be found that the relative molecular mass of the existent gum of the oxidized oil is basically unchanged compared with the existent gum of the raw oil. The relative contents of C and H decreased slightly, the relative contents of S and N increased slightly, the oxygen content increased significantly, and the hydrogen−carbon ratio decreased.

The changes in these indicators indicate that the existent gum unsaturation degree formed by the F−T synthetic crude after oxidation is further increased, and the spatial structure is further complicated. From refs 14−22, the presence of a large number of heteroatom functional groups makes the F−T synthetic crude’s existent gum can be seen, or its precursors

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Table 2. Average Relative Molecular Mass and Content of Various Elements of Different Sources of Gum

| source of gum       | relative content (%) | H/C | average relative molecular weight |
|---------------------|----------------------|-----|----------------------------------|
| FRG                 | 72.33                | 6.24| 3.07                           | 9.77| 0.797| 549               |
| FOG                 | 71.66                | 5.85| 0.41                           | 9.84| 1.41  | 760               |
| South China sea crude oil gum10 | 86.43 | 10.4 | 0.86 | 0.90 | 1.44  | 845               |
| USA Heavy oil gum11 | 58.49                | 78.13| 0.77                           | 0.65 | 1.35  | 403               |
| American shale oil gum12 | 33                | 41  | 0.1                             | 0.40 | 1.6   | 360.5             |
| gel structural unit of Fengcheng heavy oil13 | 81.7 | 9.6 | 0.45                           | 1.04 | 7.21  | 574.5             |
| Tabe atmospheric residue gum14 | 85.63 | 8.75 | 3.34                           | 1.35 | 0.93  | 627               |
| low-temperature coal tar DT-R15 | 84.2 | 8.86 | 0.37                           | 0.35 | 6.23  | 403               |
| low-temperature coal tar SM-R16 | 83.8 | 9.15 | 0.27                           | 0.58 | 6.2   | 404               |

“Low-temperature coal tar DT-R is Datong medium- and low-temperature coal tar gums. Low-temperature coal tar SM-R is Shenmu medium- and low-temperature coal tar gums.

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18780
have more force, and it is easier to generate gums. When exposed to air or in case of high oxygen content in the fuel, oxygen will induce the reaction of the heteroatom compounds, and the rate of gum formation will increase significantly.

### 3.2. FT-IR Analysis

The FT-IR method was used to characterize the characteristic groups contained in the two gums. The analysis results are shown in Table 3.

It can be seen from Figure 1 that there is an absorption peak near 1665 cm\(^{-1}\), which is attributed to the stretching vibration of carboxylic acid C\(\equiv\)O, indicating that there is a fatty branch of C\(\equiv\)O in the gum. There are absorption peaks near 1500 and 1580 cm\(^{-1}\), which are attributed to the stretching vibration peak of the aromatic ring C\(\equiv\)C, indicating the existence of an aromatic ring in the gum. There are multiple peaks of C\(\equiv\)H out-of-plane bending vibration on aromatic rings in the range of 900–650 cm\(^{-1}\), indicating the diversity and complexity of aromatic ring substituents.

### 3.3. NMR Analysis

The \(^1\)H NMR spectra of the two types of gums are shown in Figures 2 and 3. The relative molar content of various types of hydrogen in the gum is calculated from the \(^1\)H NMR spectrum of the gum and is shown in Table 4.

According to the different chemical shifts of various types of hydrogen in the hydrogen spectrum, the relative molar content of various types of hydrogens contained in the molecule can be determined. The relative molar content of hydrogen in the two gum hydrogen spectra in the chemical shift range of 0.5–1.1 ppm is low, indicating that the existing gum molecule has fewer methyl groups attached to the aromatic ring. The relative molar content of hydrogen in the chemical shift range of 1.1–2.1 ppm is relatively high, indicating that more methylene groups are connected to the aromatic ring in the existed gum molecule. The relative molar content of hydrogen in the chemical shift range of 6.5–9.5 ppm is high, indicating that there are large number of aromatic rings in the existed gum molecules. In addition, it can be found that the relative molar content of aromatic hydrogen in the existed gum of oxidized oil is about 3% higher than that of the raw oil, and the relative molar content of hydrogen directly connected to the \(\alpha\) carbon of the aromatic ring is about 7%, which indicates that in the oxidation process the gum is further aromatized and its unsaturation degree is further increased.

### 3.4. XPS Analysis

From the results of elemental analysis, it can be seen that the content of N and O in the gum is higher and the content of S is lower. Therefore, XPS Avantage

| functional group | reference value/cm\(^{-1}\) | FRG absorption peak wave/cm\(^{-1}\) | FOG absorption peak/cm\(^{-1}\) | instructions |
|------------------|-----------------------------|-------------------------------------|---------------------------------|--------------|
| C–C              | 1250–1140                   | 1220                                | 1242                            | C–C stretching vibration |
| C–H              | 1490–1350                   | 1402                                | 1401                            | C–H bending vibration |
| C–O              | 1225–1060                   | 1171                                | 1083                            | C–O stretching vibration |
| C≡O              | 1740–1650                   | 1665                                | 1655                            | C≡O stretching vibration |
| C≡C              | 1500 ± 25, 1580 ± 10         | 1500, 1583                          | 1498, 1586                      | C≡C stretching vibration |

Table 3. FT-IR Spectra of Gum

Table 4. Properties and Relative Contents of Various Types of Hydrogen in the Gum

![Infrared absorption spectra of the gum.](https://doi.org/10.1021/acsomega.0c01871)
software was used to fit the peaks of the O1s and N1s peaks to analyze the type and relative content of heteroatom-containing functional groups. The results are shown in Figures 4 and 5. The O1s and N1s center binding energies obtained by fitting the two gum XPS peaks, the corresponding functional group types, and the relative peak areas are listed in Table 5.

It can be seen from Table 5 that the oxygen elements in the two gums mainly exist in the form of C=O, C–O–C, and COO− bonds, and the relative content of COO− bonds after oxidation is significantly reduced. Carboxylic acid, as an organic acid, catalyzes the auto-oxidation process of heterocyclic nitrogen compounds in fuel oils and participates in the reaction of gum formation, which may be the reason for the further increase of the gum content after oxidation. The content of strongly basic pyridine nitrogen in gums is 32.24 and 52.84%, respectively, indicating that the nitrogen atoms in the gums mainly exist in the form of pyridine. After oxidation, the content of the nonalkaline pyrrole nitrogen in the existent gum decreased from 19.18 to 8.09%, which shows that the nonalkaline nitrogen compounds have been significantly reduced during the oxidation process. When Sobkowiak et al. studied the role of phenol, indole, and carbazole derivatives in the thermal oxidation stability of the F−T mixed fuels, they found that the indole/carbazole structure

Figure 4. Fitting results of gum peaks of raw oil derived from (a) fitting result of O1s fractional peak and (b) fitting result of N1s fractional peak.

Figure 5. Fitting results of gum peaks of oxidized oil derived from (a) fitting result of O1s fractional peak and (b) fitting result of N1s fractional peak.

| nitrogen form       | binding energy/eV | atomic ratio/% |
|---------------------|-------------------|----------------|
|                     | FGR               | POG            | FGR             | POG             |
| O                   | 531.36            | 531.70         | 24.98           | 37.22           |
| C=O                 | 532.38            | 532.72         | 34.42           | 39.75           |
| C–O–C               | 533.80            | 537.45         | 40.60           | 33.03           |
| COO−                |                   |                |                 |                 |
| N                   |                   |                |                 |                 |
| N−X (nitrous oxide) | 402.62            | 403.31         | 16.00           | 2.28            |
| Q (quaternary nitrogen) | 401.62         | 401.65         | 28.51           | 35.66           |
| N−5 (pyrrole)       | 400.56            | 400.80         | 19.18           | 8.09            |
| N−6 (pyridine)      | 399.39            | 399.70         | 32.24           | 52.84           |
exists in the diesel deposit precursor. Beaver et al.43 found that alkyl indole compounds are involved in the formation of insolubles and color during storage in diesel environments containing light cycle oil. Beaver et al.44 found that the catalytic cracking light cycle oil containing alkylphenol is harmful to the storage stability of the fuel.

With reference to earlier studies,20–22,42–44 it can be speculated that the formation process of the gum in the F–T synthetic crude is as follows. Nonalkaline nitrogen compounds in the system form peroxides when exposed to air, which in turn generates free radicals. These free radicals initiate a free radical chain reaction, during which a dehydrogenation oxidation reaction occurs and aromatic compounds are formed when the chain is terminated. Aromatic compounds will continue to produce processes similar to those described above, thereby increasing the aromaticity of the compounds. In the accelerated oxidation process, there is a stable and high content of dissolved oxygen in the system, which accelerates the formation of gums on one hand and promotes the further oxidation of the resulting gums on the other hand to form compounds with more complex spatial structures. In this procedure, the gum that has been generated will become the attachment matrix of the gum precursor, forming a gum stack.

3.5. Average Molecular Structure. Combined with the data analysis of FT-IR, NMR, elemental analysis, and relative molecular mass, the Brown–Ladner method37–40,45 was used to calculate the average molecular structure parameters of gums. The results are shown in Table 6.

As can be seen from Table 6, the carbon in the two existent gum molecules mainly exists in the form of aromatic carbon and short-chain alkyl carbon. They have a shorter average chain length and are mainly composed of aromatic rings. Compared with the raw oil gum, the oxidized oil gum’s aromaticity degree, naphthenic carbon number, total ring number, aromatic ring number, aromatic ring system total carbon number, etc. are increased to a certain extent. The decrease in the number of carbon atoms and the average chain length of the naphthenic side chain means that the side chain of the gum becomes shorter during the oxidation of the raw oil gum. It can be speculated that the complex rearrangement process may occur during the oxidation process of the raw oil gum, which makes the branch chain shorter and forms more closed loops. The basic structure of gum molecules is a molecule with fused ring aromatic hydrocarbons and alicyclic hydrocarbons, with normal or heterogeneous alkyl groups with different carbon chain lengths, and contains various heteroatoms such as N, O, S, and the corresponding group; the results obtained in this study are relatively consistent with the results of the reference.9–13 However, the existent gum molecules of the F–T synthetic crude are different from those of South China Sea crude oil, Fengcheng heavy oil, and American shale oil. Their molecular structure has the remarkable characteristics of short branched chain, small relative molecular mass, and high aromaticity.10,12,13

Combined with the above analysis data, two simplified models (a) and (c) of the possible gums are constructed in Figure 6, where (b) and (d) are the gum molecular models after structural optimization by Materials Studio software. It can be seen from (b) and (d) in Figure 6 that the two types of gum molecules have a heterohedral structure, and the functional groups containing nitrogen and oxygen are exposed to the outside and are on a cross section with less steric hindrance. These nitrogen- and oxygen-containing functional groups often have strong reactivity. Therefore, such a spatial configuration allows the gum molecules to further react.

3.6. Aggregation State. To simulate the aggregation state of gums in the mixed solvent of acetone and toluene, a periodic solvent cubic box was constructed in the amorphous cell module, and two sets of experiments were conducted. The first group uses three gum molecules as solutes. The molar ratio of solute to solvent is 1:10, and the molar ratio of acetone to toluene is 1:1. The second group uses 3 gum molecules as the solute, with the molar ratio of solute to solvent of 3:32 and the molar ratio of acetone to toluene of 1:3. Figures 7 and 8 are models of the above simulation system before and after kinetic annealing treatment at 1500 ps. The initial state is a random state. For the convenience of observation, the solvent molecules have been deleted.

It can be seen from Figures 7 and 8 that gums accumulate in the mixed solvent of acetone and toluene, and all exhibit a partial T-shaped stacking method. The possible causes of this aggregation form are as follows. First, there are strong π–π stacking and hydrogen bonding forces in gum molecules. Second, the oxygen atoms existing in acetone form a hydrogen bond between the gum molecules, while the main body of toluene is the benzene ring, which can produce the π–π stacking effect between the gum molecules. This all weakens the force of gum molecules to a certain extent. In addition, it can be seen that as the toluene content in the mixed solvent increases, the degree of dispersion of gum molecules in the mixed solvent becomes larger. It can be inferred that the strong

| parameter | symbol | calculating formula | FRG | FOG |
|-----------|--------|---------------------|-----|-----|
| aromaticity | f_a | C/H − H_a/2 − H_p/2 − H_r/3 | 0.69 | 0.73 |
| aromatic ring substitution | σ | H_a/2 + O/2 + H_r | 0.35 | 0.39 |
| number of aromatic carbon atoms | C_A | C_a | 22.83 | 23.60 |
| naphthenic carbon number | C_p | 0.01 × C × 54.3 (H_c/H_p + 0.1) | 4.76 | 6.77 |
| number of carbons in the naphthenes side chain | C_p | C − C_A − C_n | 5.50 | 1.96 |
| the total number of ring | R | C − H/2 + 1 − (C_L)/2 | 5.54 | 5.54 |
| aromatic ring number | L | (C_A − 2)/4 | 5.21 | 5.40 |
| the total number of carbon atoms outside the aromatic ring system | C_l | H_p/2 + H_a | 15.71 | 17.40 |
| the total number of carbon atoms substituted outside the aromatic ring | C_o | C_l − H_p | 3.01 | 4.05 |
| the average chain length | L | C_o/C_p + H_a/C_p + C_o/C_p | 4.28 | 3.00 |
van der Waals interaction between toluene and gum molecules in the solvent causes the van der Waals interaction within the gum molecules to be destroyed. Therefore, as the content of nonpolar solvents in the solvent increases, the degree of dispersion of gum molecules in the mixed solvent becomes larger.

4. CONCLUSIONS

(1) The existent gum of F-T synthetic crude is a polar molecule containing heterocyclic aromatic hydrocarbons, short carbon chain alkanes, and heteroatoms such as N, O, and S. The average molecular weight of FRG is 549, and the average molecular weight of FOG is 546. Combined with nuclear magnetic analysis, it can be found that the content of aromatic carbon and alkyl carbon in the colloidal molecule is higher, and the content of naphthenic carbon is lower. The O element in the gum mainly exists in the form of ethoxy group, carbonyl group and carboxyl group, and the N element mainly exists in the form of pyridine. The main structure of the two types of gums is composed of aromatic rings.

(2) Judging from the content of nonalkaline nitrogen compounds in the existent gums of the two F−T synthetic crude, it can be seen that this type of content has been significantly reduced during the gum oxidation process, which is formed with the air oxygen, or dissolved oxygen in fuel free radicals are an important step in the process of gum formation.

(3) The existent gum of the F−T synthetic crude in the mixed solvent with a molar ratio of acetone and toluene of 1:3 shows a partial T-shaped stacking method; however, as the content of nonpolar solvents in the solvent increases, the solubility of gum molecules in the mixed solvent increases.

(4) The work done so far does not intuitively reveal the existent gum formation mechanism of the F−T synthetic
crude. The next stage still needs to use Fourier ion cyclotron resonance mass spectrometry (ESI FT-ICR MS), sulfur chemiluminescence gas phase chromatography (GC-SCD), nitrogen chemiluminescence gas chromatography (GC-NCD), and other analytical methods at the molecular level to study the role of heteroatom compounds in the formation of such gums.

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**Notes**

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