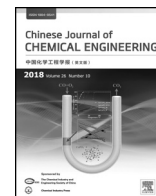




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Article

Insight into the structural features of organic species in Fushun oil shale *via* thermal dissolution☆Shengkang Wang¹, Xianyong Wei^{1,2,*}, Zhimin Zong¹¹ Key Laboratory of Coal Processing and Efficient Utilization, Ministry of Education, China University of Mining & Technology, Xuzhou 221116, China² State Key Laboratory of High-efficiency Coal Utilization and Green Chemical Engineering, Ningxia University, Yinchuan 750021, China

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ABSTRACT

Fushun oil shale (FOS) was subjected to thermal dissolution (TD) under different conditions. The results show that the optimal solvent, temperature, time, and ratio of solvent to FOS are ethanol, 300 °C, 2 h, and 5 ml·g⁻¹, respectively and the corresponding yield of the soluble portion (SP) is 32.2% (daf), which is much higher than the oil content of FOS (ca. 6%), suggesting that TD in ethanol is an excellent way to extract organics from FOS. According to 3 direct analyses, aliphatic moieties in FOS are the most abundant followed by C—O-containing moieties and each cluster in FOS has 3 conjugated aromatic rings on average with fewer substituents. According to the analysis with a gas chromatograph/mass spectrometer, alkanes are predominant in all the SPs. A number of alkenes were identified in the SPs from the TD, while none of the alkenes were detected in acetone-SP obtained at room temperature, implying that the TD can destroy the π - π and intertwining interactions between alkenes and macromolecular structures in FOS. Moreover, a small amount of alkyl-substituted phenols and alkoxy-substituted phenols were detected in ethanol-SP from the TD, which could be the products from ethanolizing the macromolecular moiety of FOS.

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1. Introduction

Oil shale (OS) is regarded as an important alternative energy in the 21st century for its abundant reserve and feasibility of exploitation and utilization. The OS reserves in China are up to 4.76×10^{10} t (converted to the content of shale oil) according to the research in 2006 [1]. About 85% of OS reserves were distributed in Jilin, Guangdong, and Liaoning provinces in China [1, 2]. At present, most of the OS was converted to energy *via* pyrolysis or combustion [3–5] with vast energy and the emission of harmful gases. Therefore, it is necessary to understand the structural feature of OS for developing the value-added utilization of OS.

Solvent extraction [6–8] and thermal dissolution (TD) [9–12] are important methods to extract organics from coals or their derivatives. For instance, more than 10% of organic portion was extracted from Geting bituminous coal at room temperature [6]. Shui *et al.* [9] investigated the TD of Shenfu coal at different temperatures in different solvents. They found that the highest yield of 56% was obtained in 1-methylnaphthalene at 360 °C. However, only few investigations are issued on the TD of OSs [13].

The direct characterization instruments can directly and conveniently analyze the whole, unaltered, and solid coals and OSs. Fourier transform infrared (FTIR) spectrometer could reveal the information of organic functional groups in coals [6, 14]. The solid-state ¹³C nuclear magnetic resonance (SS ¹³C NMR) spectrometer is usually used to obtain the information of carbon skeletal structure in coals [15, 16] and OSs [17]. X-ray photoelectron spectrometer (XRPES) is also a powerful tool to analyze the forms of carbon, oxygen, sulfur, and nitrogen in coals and OSs [15–18]. In addition, a gas chromatograph/mass spectrometer (GC/MS) is widely applied to detect organic species in coals or their derivatives [19, 20], petroleum [21–23] and OSs [24, 25].

In this paper, Fushun OS (FOS) was subjected to TD in cyclohexane, methanol, ethanol, and isopropanol. Meanwhile, time, temperature, and ratio of solvent to FOS (solvent/FOS) were also investigated to discover the optimal conditions for the TD of FOS. FOS and the soluble portions (SPs) were analyzed with a variety of tools to understand the structural and compositional characteristics of FOS.

2. Materials and Methods

2.1. Materials

FOS was collected in Fushun, Liaoning, China. Table 1 displays its proximate and ultimate analyses. The FOS was milled and sieved to a particle size of <74 μ m followed by desiccation in an oven at 80 °C for 24 h before use. Acetone, cyclohexane, methanol, ethanol,

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Table 1
Proximate and ultimate analyses (wt%) of FOS

Proximate analysis/%			Ultimate analysis (daf)/%					H/C
M_{ad}	A_d	VM_{daf}	C	H	N	S	O ^①	
2.28	68.25	77.40	47.22	8.13	2.73	1.68	40.25	2.05

① By difference.

and isopropanol used in this experiment are analytical reagents and were distilled prior to use.

2.2. Experimental procedure

FOS (2 g) and ethanol (10–25 ml) were added to a 100 ml stainless steel and magnetically stirred autoclave. Then, using N_2 to replace the air inside the reactor of the autoclave and charging the pressure of N_2 to 1 MPa, the autoclave was heated to a prescribed temperature (260–320 °C) and kept at the temperature for an indicated period of time (0.5–2.0 h) followed by cooling the reactor to room temperature. Subsequently, the reaction mixture was taken out and exhaustively extracted with acetone under ultrasonic radiation to obtain ethanol-SP (ESP). Similarly, the cyclohexane-SP (CHSP), the methanol-SP (MSP), and the isopropanol-SP (IPSP) were obtained based on the above method, respectively. In addition, as a comparison, FOS (2 g) was exhaustively extracted with acetone at room temperature to afford the acetone-SP (ASP). The yield (Y) of each soluble portion was calculated as the mass ratio of the extracts (m_E) to FOS on a dry and ash-free basis ($m_{FOS, daf}$); i.e., $Y = m_E / m_{FOS, daf}$.

2.3. Analytical methods

FOS was characterized with a FTIR spectrometer, SS ^{13}C NMR, and XRPES. The FTIR spectrum was recorded on a Nicolet Magna IR-560 FTIR spectrometer at a resolution of 8 cm^{-1} with a wavenumber region of $4000\text{--}400\text{ cm}^{-1}$. The SS ^{13}C NMR analysis was conducted on a Bruker Avance III spectrometer equipped with a 4.0 mm cross-polarization magic angle spinning double-resonance probhead and operated at a ^{13}C frequency of 100.63 MHz at room temperature. The spectral width, recycle delay time, and contact time were set to 10 kHz, 0.5 s, and 1 ms, respectively. Curve fitting of the SS ^{13}C NMR spectrum was performed using the PeakFit software to obtain the distributions of different carbon types in FOS. The surface elemental compositions of FOS were analyzed by a Thermo Fisher ESCALAB 250Xi XRPES equipped with a monochromatic Al K_{α} X-ray source and operated at 150 W. All electron binding energies were corrected by references [15, 26] to the C 1s peak at 284.8 eV for binding energy calibration. Peak fitting of XRPES spectra was performed using XRPES PeakFit software.

All the SPs were detected by an Agilent 7890/5975 GC/MS, which was equipped with a DB-35MS capillary column (cross-link 5% PH ME

siloxane, 60 m length, 0.25 mm inner diameter, 0.25 μm film thickness) and a quadrupole analyzer with a m/z range from 33 to 500. The split ratio was 20:1 and the capillary column was heated at a rate of $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ from 60 to 300 °C and held at 300 °C for 5 min. Data acquired were processed using ChemStation software. Compounds were identified by comparing mass spectra with NIST11 library data. Each sample was analyzed at least 2 times and the results are basically consistent.

3. Results and Discussion

3.1. Direct characterization of FOS

As Fig. 1 demonstrates, the dominant absorbance band around 1032 cm^{-1} and its minor shoulder bands around 1097 cm^{-1} and 1009 cm^{-1} are assigned to the C—O vibrations, suggesting the presence of abundant C—O moieties in FOS corresponding to high oxygen content in Table 1. The stronger absorbances around 2924 cm^{-1} , 2852 cm^{-1} , and 1458 cm^{-1} are ascribed to aliphatic moieties (AMs), indicating the rich existence of AM-containing species in FOS. The absorbance around 1628 cm^{-1} originates from the C=C band stretching vibration and the absorbances around 798, 778, and 695 cm^{-1} generate from the aromatic C—H out-of-plane bending vibrations. Moreover, the strong absorbances around 912, 536, and 467 cm^{-1} attributed to mineral matter are consistent with the high ash of FOS (Table 1).

Usually, SS ^{13}C NMR spectra of coals could be divided into 3 chemical regions: aliphatic carbons ($0\text{--}90\text{ mg}\cdot\text{L}^{-1}$), aromatic carbons ($90\text{--}170\text{ mg}\cdot\text{L}^{-1}$), and carbonyl carbons ($170\text{--}220\text{ mg}\cdot\text{L}^{-1}$) [14, 15]. As exhibited in Fig. 2, the spectrum of FOS can be classified into 16 individual peaks through curve fitting. These peaks are attributed to 3 types of aliphatic, aromatic, and carbonyl carbon species with the molar contents of 64.34%, 28.79%, and 6.87%, respectively (Tables 2 and 3), indicating that the carbon skeletal structure of FOS mainly consists of aliphatic and aromatic carbons and the aliphatic carbon is more than twice of aromatic carbon.

In the aliphatic carbon region, the dominant peak at $26.6\text{ mg}\cdot\text{L}^{-1}$ generated from methylene carbons could be ascribed to methylene in AMs and the stronger peaks around 12.1 and $40.0\text{ mg}\cdot\text{L}^{-1}$ originate from aliphatic methyl (f_{al}^1) and methine (f_{al}^3), respectively, indicating that abundant AMs exist in FOS corresponding to FTIR analysis. Noteworthy, several weak peaks ranged from 55 to 81 ppm are attributed to aliphatic C—O belonging to aliphatic alcohols and/or ethers. At the aromatic band ($101\text{--}165\text{ mg}\cdot\text{L}^{-1}$), the main aromatic carbons are protonated aromatic (f_a^H) and aromatic bridgehead (f_a^B) carbons, followed by aromatic branched (f_a^S) and oxygen-substituted aromatic (f_a^O) carbons (Table 2). In addition, the carbonyl carbons ($176\text{--}217\text{ mg}\cdot\text{L}^{-1}$) with a total molar content of 6.87% indicate the presence of small amounts of carboxylic acids (CAs), esters, ketones, or aldehydes in FOS.

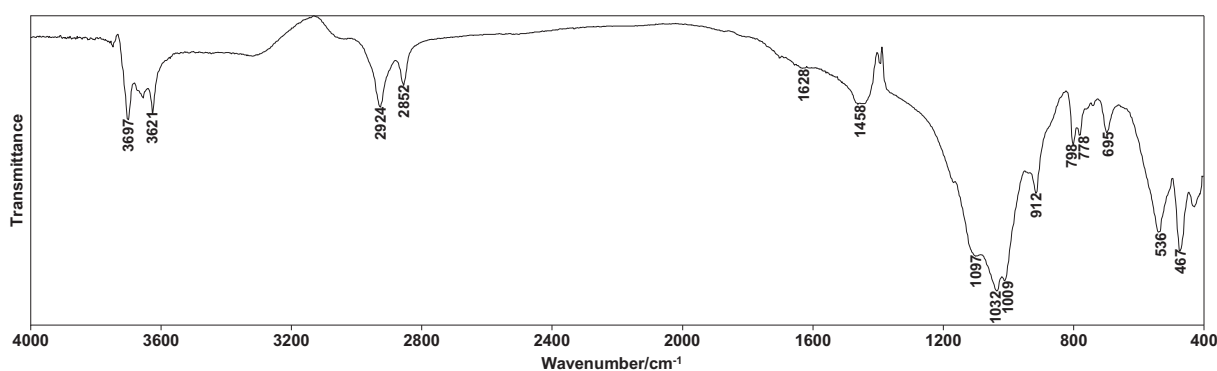


Fig. 1. FTIR spectrum of FOS.

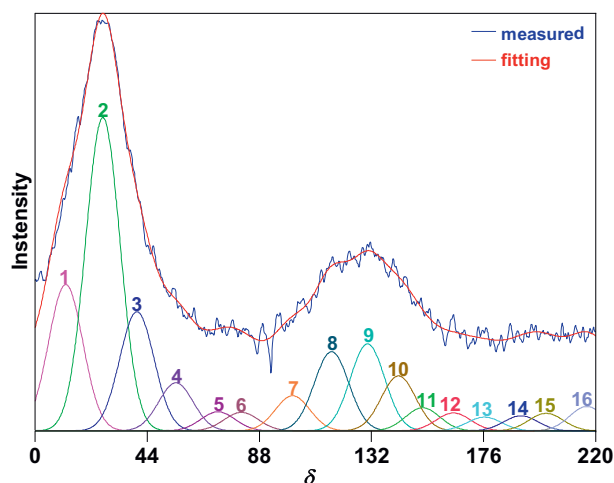


Fig. 2. SS ^{13}C NMR spectrum and the fitting curves of FOS.

Table 2

Distribution of different carbon types in FOS determined by SS ^{13}C NMR analysis

Peak	Chemical shift/ $\text{mg} \cdot \text{L}^{-1}$	Carbon type	Molar content/%
Aliphatic			
1	12.1	f_{al}^1	14.17
2	26.6	f_{al}^2	30.33
3	40.0	f_{al}^3	11.54
4	55.3	f_{al}^4	4.66
5 & 6	71–81	f_{al}^5	3.64
Aromatic			
7 & 8	101–117	f_{a}^7	11.07
9	130.4	f_{a}^9	8.42
10	142.6	f_{a}^{10}	5.32
11 & 12	152–165	f_{a}^{11}	3.98
Carbonyl			
13 & 14	176–191	$f_{\text{a}}^{\text{C}1}$	2.80
15 & 16	200–217	$f_{\text{a}}^{\text{C}2}$	4.07

Note: f_{al}^1 , aliphatic CH_3 ; f_{al}^2 , aliphatic methylene ortho to methyl; f_{al}^3 , methane; f_{al}^4 , oxymethylene; f_{al}^5 , oxy-methylene & oxy-quaternary; f_{a}^7 , protonated aromatic carbon; f_{a}^9 , aromatic bridgehead; f_{a}^{10} , aromatic branched; f_{a}^{11} , oxygen-substituted aromatic; $f_{\text{a}}^{\text{C}1}$, carbonyl in carboxyl and ester; $f_{\text{a}}^{\text{C}2}$, carbonyl in ketone and aldehyde.

Table 3

Structural parameter values (%) of FOS determined by SS ^{13}C NMR analysis

f_{a}	f_{al}	f_{a}^{C}	χ_{b}	C_{n}	σ
28.79	64.34	6.87	29	787	32

Note: Aromaticity index $f_{\text{a}} = f_{\text{a}}^7 + f_{\text{a}}^9 + f_{\text{a}}^{10} + f_{\text{a}}^{11}$; aliphaticity index $f_{\text{al}} = f_{\text{al}}^1 + f_{\text{al}}^2 + f_{\text{al}}^3 + f_{\text{al}}^4 + f_{\text{al}}^5$; ratio of carbonyl carbon $f_{\text{a}}^{\text{C}} = f_{\text{a}}^{\text{C}1} + f_{\text{a}}^{\text{C}2}$; molar fraction of aromatic bridgehead carbon $\chi_{\text{b}} = f_{\text{a}}^7/f_{\text{a}}$; average carbon number in methylene chain $C_{\text{n}} = (f_{\text{al}}^2 + f_{\text{al}}^3)/f_{\text{al}}$; average substituted degree of aromatic ring $\sigma = (f_{\text{a}}^9 + f_{\text{a}}^{10})/f_{\text{a}}$.

As Table 3 displays, some important parameters, such as the molar fraction of aromatic bridgehead carbon (χ_{b}), were calculated, which are generally used to estimate the aromatic cluster size. The χ_{b} of FOS is 0.29 corresponding to anthracene or phenanthrene, suggesting that the average number of aromatic rings per cluster in FOS is 3. The average carbon number in methylene chain (C_{n}) is 7.87, showing that most of the side-chains or bridged bonds in the carbon skeletal structure of FOS are longer compared to previous researches [14, 15, 27]. The average substituted degree of aromatic ring in FOS is ca. 0.32, implying that the average number of substituents on each aromatic ring is 1.9.

As demonstrated in Fig. 3 and Table 4, 5 peaks at 284.8, 285.3, 286.3, 287.5, and 289.0 eV in the XRPES C 1s spectrum of FOS were fitted

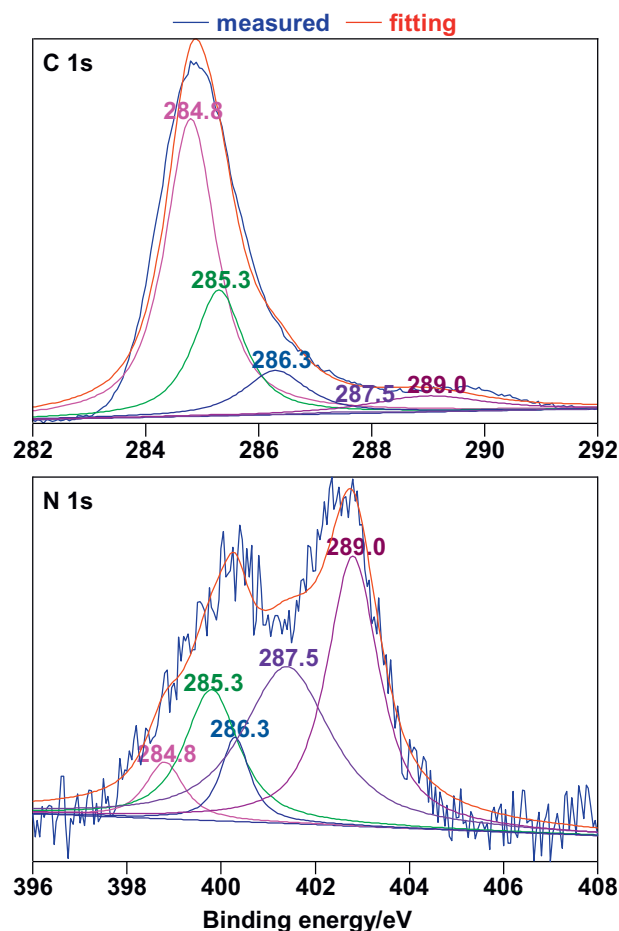


Fig. 3. X-ray photoelectron spectrum and their fitting curves of FOS.

Table 4

Distributions of carbon and nitrogen forms in FOS from the analysis with XRPES

Elemental peak	Functionality	Binding energy/eV	Molar content/%
C 1s	C—C	284.8	57.80
	C—H	285.3	24.03
	C—O	286.3	10.64
	C=O	287.5	0.51
	COO	289.0	7.02
N 1s	Pyridinic	398.8	5.47
	Amino	399.8	17.94
	Pyrolic	400.3	6.24
	Quaternary	401.4	34.72
	Chemisorbed nitrogen oxides	402.8	35.63

[15, 17], corresponding to C—C, C—H, C—O, C=O, and COO moieties, respectively. The molar content of C—C and C—H moieties is over 80%, indicating that large amounts of AMs exist in FOS, which is in accordance with FTIR and ^{13}C NMR analyses. The C—O and C=O groups are the main form of oxygen element on the surface of FOS, which was also confirmed by ^{13}C NMR analysis. In the N 1s spectrum, chemisorbed nitrogen oxides and quaternary nitrogen are the most abundant in all the nitrogen structures, followed by amino, pyrrolic, and pyridinic nitrogens.

3.2. SP yields

Referring to previous reports [1, 2], the oil content of FOS was ca. 6% (wt%). As Fig. 4 displays, the yields of ASP, CHSP, MSP, ESP, and IPSP are

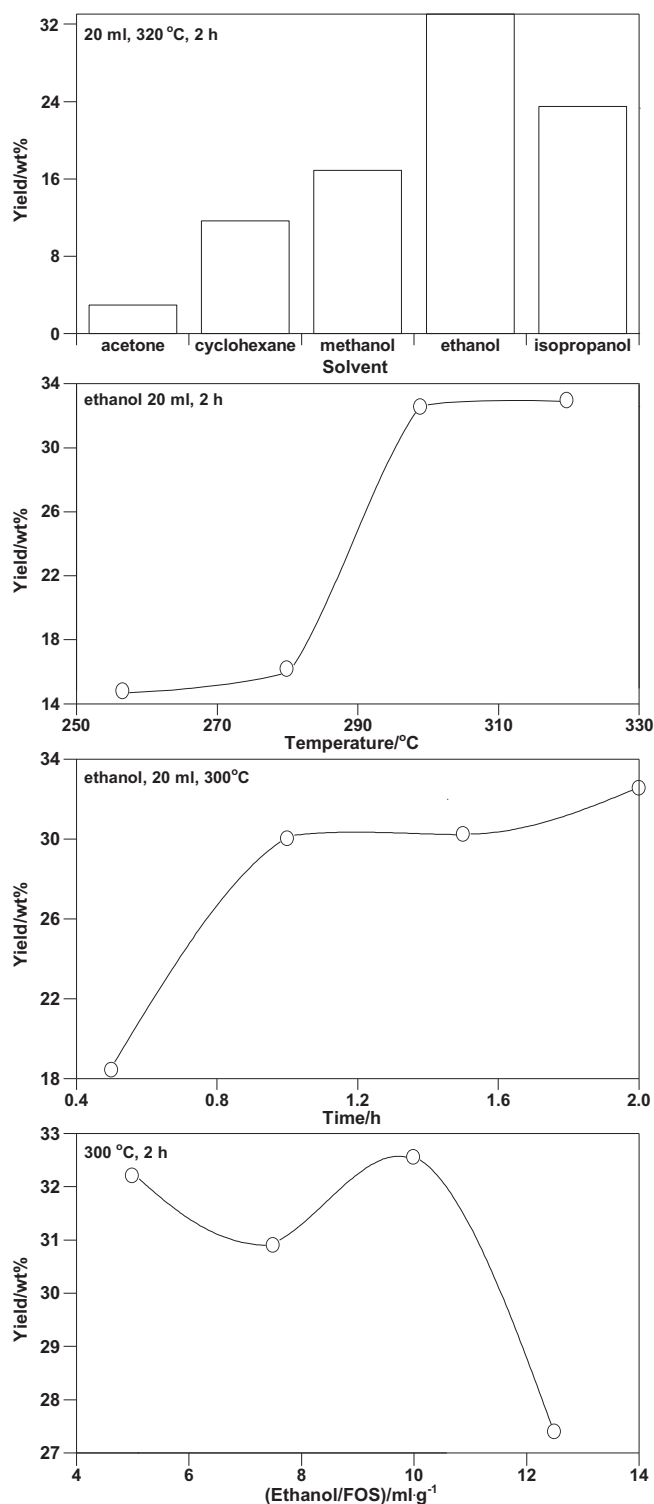


Fig. 4. Effects of solvent, temperature, time, and ethanol/FOS on the SP yields from the TD/alkanolysis of FOS.

3.2%, 11.6%, 16.8%, 32.9%, and 23.5%, respectively, indicating that the optimal solvent is ethanol. The yield rapidly increases with increasing temperatures from 260 °C to 300 °C, then slowly increases with raising temperatures from 300 °C to 320 °C, showing that 300 °C is the suitable temperature because of the only 0.3% difference of the yields between 300 °C and 320 °C. Prolonging time from 0.5 h to 1 h led to a rapid increase in the yield, while the yield gradually increases with prolonging time from 1 h to 2 h and reached the peak at 2 h with a yield of

32.6%. Therefore, the optimal time is 2 h. Interestingly, with increasing ethanol/FOS from 5 to 7.5 ml·g⁻¹, the yield decreases from 32.2% to 30.9%, then increases to 32.6% at the ratio of 10 ml·g⁻¹ and further decreases to 27.4% at ethanol/FOS of 12.5 ml·g⁻¹, indicating that adding more solvents may not be beneficial to the yield of FOS through the TD at higher temperature and the appropriate ethanol/FOS is 5 ml·g⁻¹.

3.3. Molecular compositions in SPs

As exhibited in Figs. S1–S5 and Tables S1–S32 (see in Supporting Information), a total of 309 compounds were determined in the SPs from the analysis with GC/MS. They were divided into normal alkanes (NAs, Table S1), branched alkanes (BAs, Table S2), cyclanes (Table S3), alk-1-enes (Table S4), alk-2-enes (Table S5), alk-3-enes (Table S6), alk-5-enes (Table S7), alk-6-enes (Table S8), alk-7-enes (Table S9), alk-9-enes (Table S10), alk-11-enes (Table S11), other alkenes (OAs, Table S12), cyclenes (Table S13), alkyl-substituted benzenes (ASBs, Table S14), diarylmethanes (DAMs, Table S15), indane and alkyl-substituted indanes (I & ASIs, Table S16), tetralin and alkyl-substituted tetralins (T & ASTs, Table S17), methyl-substituted naphthalenes (MSNs, Table S18), alkyl-substituted phenanthrenes (ASPs^I, Table S19), other substituted arenes (OSAs, Table S20), alkyl-substituted phenols (ASPs^{II}, Table S21), alkoxy-substituted arenes (ASAs, Table S22), methoxy-substituted phenols (ASPs^{III}, Table S23), ketones (Table S24), alkanoic acids (AAs, Table S25), methyl alkanoates (MAs, Table S26), ethyl alkanoates (EAs, Table S27), ethyl alkenoates (EAs', Table S28), other esters (OEs, Table S29), alkyl-substituted pyridines (ASPs^{IV}, Table S30), amides (Table S31), and piperidine derivatives (PDs, Table S32).

Fig. 5 demonstrates that alkanes including NAs and BAs take the largest share in each sample with relative content (RC) over 45.0%, suggesting that alkanes, especially NAs, are the main compounds in FOS, corresponding to the ¹³C NMR and XRPES analyses of FOS. In ASP, alkanes with a RC of 81.2% are dominant followed by cycloalkanes and amides. Interestingly, no alkenes were detected in ASP, while many alkenes, particularly *n*-alkenes, were identified in other SPs. The π - π and intertwining interactions between alkenes and macromolecular structure in FOS should be responsible for no alkenes determined in ASP. Nevertheless, TD with higher temperature could break these interactions and promote the release of alkenes. Notably, the RC of alk-*n*-enes (*n* = odd number) are much more than alk-*m*-enes (*m* = even number), indicating that the double bond position of alkenes in FOS has an odd number predominance.

Most MAs were detected in MSP, while only 1 and 3 MAs were determined in ESP and LPSP, respectively, as illustrated in Fig. 5 and Tables S26 and S29. EAs were only determined in ESP (Tables S27–S29) and none of MAs and EAs were detected in ASP and CHSP, suggesting that the presence of MAs and EAs may generate from the transesterification reaction [12, 28]. As Fig. 6 shows, the formation of alkanoates and alkenoates can be ascribed to the nucleophilic attack of methoxy in methanol or ethoxy in ethanol on the C* atom on macromolecular moieties and subsequent transfer of CH₃ or C₂H₅ to O* atom leads to the C*—O* bond cleavage. The lower charge density of the C* atom is positively charged and the O* atom is negatively charged. Therefore, the C* atom is easily attacked by CH₃O— or C₂H₅O— groups and thereby facilitates the formation of MEs and EEs. Furthermore, these esters may generate from the esterification reaction of CAs and methanol or ethanol because some CAs may exist in OS [29], which was also proved with SS ¹³C NMR and XRPES analyses. The results also confirm that rich C—O moieties exist in the macromolecular structure of FOS, which is consistent with the 3 direct characterizations.

Besides, many arenes with 1–3 rings were detected in SPs and ASBs, DAMs, I & ASIs, T & ASTs, and MSNs are the main group components. Noteworthy, lots of ASPs^{II} were identified in MSP and ESP, especially in ESP (Table S21), while no ASPs^{II} were identified in ASP and CHSP. Likewise, most of ASAs (Table S22) and ASPs^{III} were detected in ESP

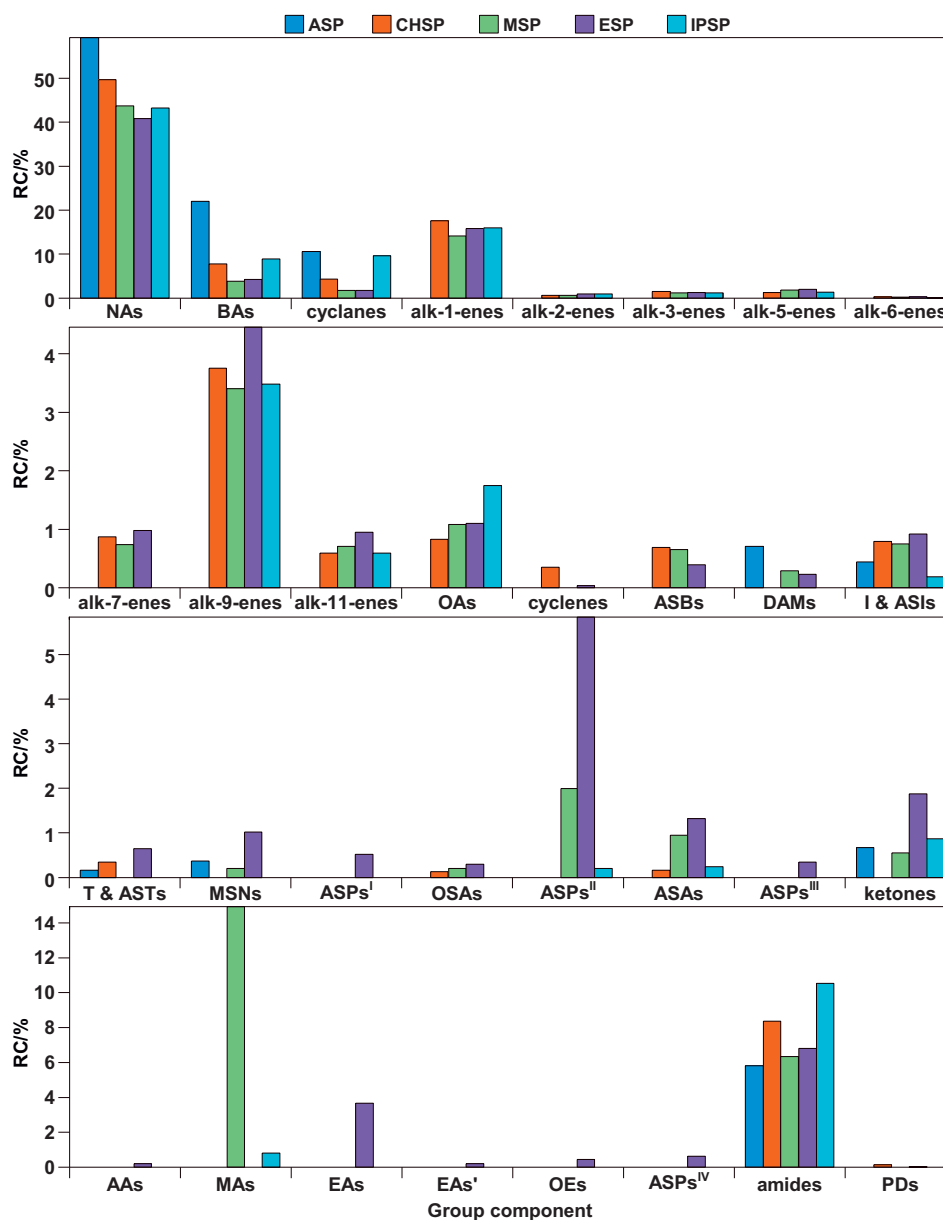


Fig. 5. Distribution of group components in SPs.

(Tables S23), guessing that the ethoxy group in ethanol has higher nucleophilicity. That's because the electron-donating ability of ethoxy group is stronger than methoxy group and steric hindrance of isopropoxy group is larger than ethoxy group. As displayed in Fig. 7,

the alkoxy group can attack the $^*C$ atom on macromolecular moieties and, subsequently, hydrogen transfers to the O^* atom, leading to the cleavage of $^*C-O^*$ to produce ASP^{II} or ASP^{III} . As for ASAs (Fig. 7), the mechanism is the same as MAs and EAs. Moreover, lots of amides

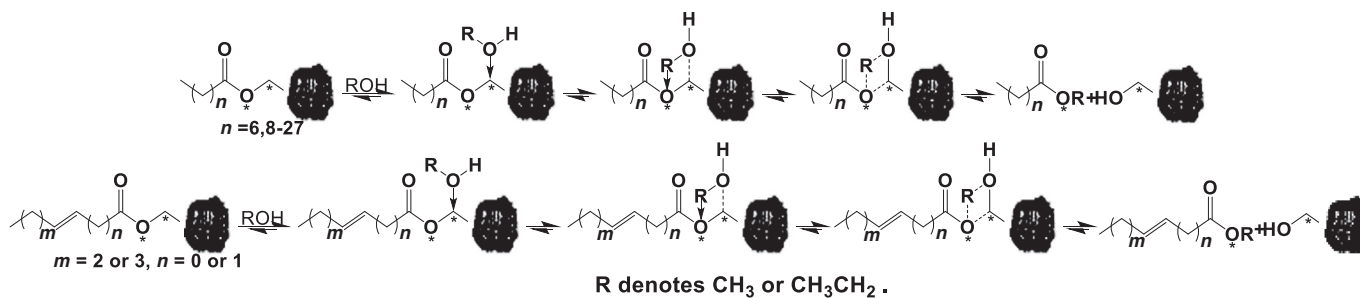


Fig. 6. Possible pathways for the formation of alkanoates and alkenoates during the alkanolyses.

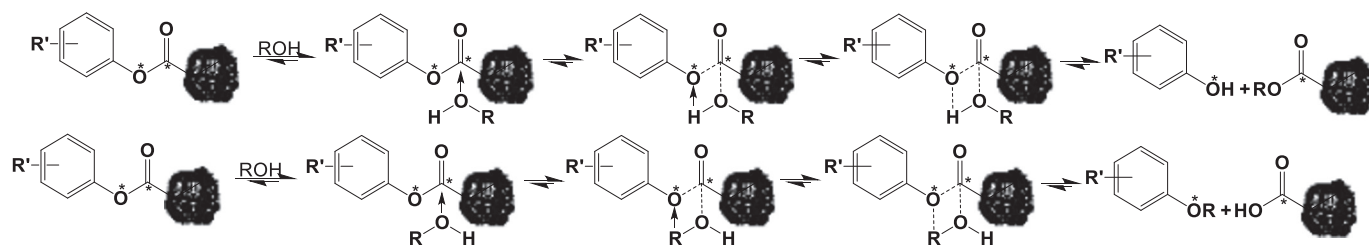


Fig. 7. Possible pathways for the formation of APs, AOPs, and AOBs during the alkanolyses.

were detected in SPs, which was also proved in FOS from the analysis with XRPES.

4. Conclusions

The optimal solvent, temperature, time, and solvent/FOS are ethanol, 300 °C, 2.0 h, and 5 ml·g⁻¹, respectively and the corresponding yield of FOS is 32.9% (daf). On the basis of FTIR, SS ¹³C NMR, and XRPES analyses, AM is the main portion in FOS and abundant C—O moieties exist in FOS. In addition, each cluster in FOS has three aromatic rings on average and the average number of substituents on each aromatic ring is 1.9 from the analysis with ¹³C NMR. The GC/MS analysis exhibits that alkanes consisting of NAs and BAs are the richest portion in SPs, especially NAs. Many alkenes were identified in SPs except in ASP and rich amides were detected in all SPs. Moreover, large amounts of MAs and EAs were determined, implying the nucleophilic attack of CH₃O⁻ in methanol and C₂H₅O⁻ in ethanol on the bridged bonds of *C—O* in FOS.

Nomenclature

AAs	alkanoic acids
ASAs	alkoxy-substituted arenes
ASBs	alkyl-substituted benzenes
ASP	acetone-soluble portion
ASPs ^I	alkyl-substituted phenanthrenes
ASPs ^{II}	alkyl-substituted phenols
ASPs ^{III}	alkoxy-substituted phenols
ASPs ^{IV}	alkyl-substituted pyridines
BAs	branched alkanes
CHSP	cyclohexane-SP
EAs	ethyl alkanoates
EAs'	ethyl alkenoates
ESP	ethanol-SP
FOS	Fushun OS
FTIR	Fourier transform infrared
f _{al} ¹	aliphatic CH ₃
f _{al} ²	aliphatic methylene ortho to methyl
f _{al} ³	methine
f _{al} ⁰¹	oxymethylene
f _{al} ⁰²	oxymethylene & oxyquaternary
f _a ^H	protonated aromatic carbon
f _a ^B	aromatic bridgehead
f _a ^S	aromatic branched
f _a ⁰	oxygen-substituted aromatic
f _a ^{C1}	carbonyl in carboxyl and ester
f _a ^{C2}	carbonyl in ketone and aldehyde
GC/MS	gas chromatograph/mass spectrometer
I & ASIs	indane and alkyl-substituted indanes
IPSP	isopropanol-SP
MAs	methyl alkanoates
MSNs	methyl-substituted naphthalenes
MSP	methanol-SP
NAs	normal alkanes
OAs	other alkenes
OEs	other esters

OS	oil shale
OSAs	other substituted arenes
PDs	piperidine derivatives
RC	relative content
solvent/FOS	ratio of solvent to FOS
SPs	soluble portions
SS ¹³ C NMR	solid-state ¹³ C nuclear magnetic resonance
TD	thermal dissolution
T & ASTs	tetralin and alkyl-substituted tetralins
XRPES	X-ray photoelectron spectrometer

Supplementary Material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cjche.2018.05.013>.

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