Fuel Processing Technology 176 (2018) 138–145

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Research article

New insight into the chemical structures of Huadian kerogen with supercritical ethanolysis: Cleavage of weak bonds to small molecular compounds

Qing Liu[a], Yucui Hou[b], Weize Wu[a,*], Qian Wang[a], Shuhang Ren[a], Qingya Liu[a]

[a] *State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China*
[b] *Department of Chemistry, Taiyuan Normal University, Jinzhong, Shanxi 030619, China*

ARTICLE INFO

Keywords:
Oil shale kerogen
Ethanolysis
Weak bonds
Small molecular compounds
Structural characteristics

ABSTRACT

Oil shale is a potential alternative fossil energy source. The chemical structure of oil shale kerogen is the basis of its application, presently for retorting to yield shale oil and gas. Supercritical ethanolysis is a kind of chemical extraction which can effectively depolymerize organic matter like coal and lignin through breaking some weak bonds. In this work, new insights into weak bonds (including O-containing, N-containing and S-containing functional groups) of the chemical structures of Huadian kerogen (HDK) were obtained with supercritical ethanolysis, and the resulted products, small molecular compounds (SMCs), were identified. It was found that, after ethanolysis at 375 °C, 87.4% of HDK was converted by breaking the weak bonds to SMCs, including aliphatic acid esters, aliphatic acids, alkanes, alcohols, aromatics, N-containing organic compounds (NCOs), and S-containing organic compounds (SCOs). In the SMCs, there are 52.0% aliphatic acid esters and aliphatic acids with carbon numbers from 4 to 26, 11.4% alkanes with carbon numbers from 14 to 22, 19.1% aromatic compounds with single-ring and double-ring aromatic clusters, 5.4% alcohols, 5.0% NOCs, 1.9% SCOs, and 5.4% biomarkers. FTIR and ^{13}C NMR were used to characterize the changes of HDK and its residues, which further demonstrate that the SMCs are present and connected with weak bonds to solid aromatic clusters insoluble in ethanol. During the pyrolysis of oil shale, these weak bonds are first broken and the above SMCs are produced in molecular or radical states, which are the most compounds from the primary reactions and readily undergo the second reactions to yield oil and gas.

1. Introduction

Oil shale is commonly defined as a fine-grained sedimentary rock containing kerogen that can yield substantial amounts of oil and combustible gas upon destructive distillation [1]. Due to its abundance, oil shale is considered as a potential alternative fossil energy. Kerogen plays a central role among the thermochemical reactions of oil shale, in retorting or burning utilization, depending on its depositional history and the resulting components [2]. It is well known that the application of a substance is dependent on its properties and its properties on its chemical structures. Hence, it is of great significance to study on the chemical structure of kerogen. Many strategies, including pyrolysis [3–6], oxidation [7–10], hydrolysis [11] and extraction [12], have been explored for study of its chemical structure for the past decades.

The pyrolysis of oil shale is the most direct chemical method to probe kerogen's structure, which can be regarded as two steps: generation of free radicals after the cleavage of covalent bonds (called primary reactions) and coupling of free radical fragments to form volatiles (shale oil and gas) and char (called secondary reactions) [13,14]. Unfortunately, it is hard to prevent the occurrence of the secondary reactions (like condensation) and selectively break covalent bonds, resulting in the products that are not representative of the original structure. Therefore, limited information on the content and composition of primary products, which are obtained by breaking covalent bonds in kerogen, can be found in the literature. As we know, kerogen of oil shale is a high-molecular-weight substance, whose structure contains both units with an aromatic ring or more and units with the open chains of atoms. The aliphatic and cyclic fragments of kerogen are connected with each other by means of O-, S-, N-containing bridges such as ester, ether and thioether bridges, which are called weak bonds, or by C—C bonds, which are stronger than the previous weak bonds [15,16]. During pyrolysis of oil shale, these weak bonds are first broken, and primary compounds or radical compounds are yielded, which can be called the primary reactions. These radical compounds

---

[*] Corresponding author.
E-mail address: wzwu@mail.buct.edu.cn (W. Wu).

https://doi.org/10.1016/j.fuproc.2018.03.029
Received 7 February 2018; Received in revised form 21 March 2018; Accepted 24 March 2018

Table 1
Proximate and ultimate analyses of Huadian oil shale.

Proximate analysis/%			Ultimate analysis/%				
M_{ad}	A_{ad}	V_{ad}	C_{ad}	H_{ad}	N_{ad}	S_{ad}	O_{ad}[a]
2.7	2.9	69.5	68.9	7.6	1.5	2.8	13.6

ad: air-dry basis; *M*: moisture; *A*: ash; *V*: volatile matter content.
[a] By difference.

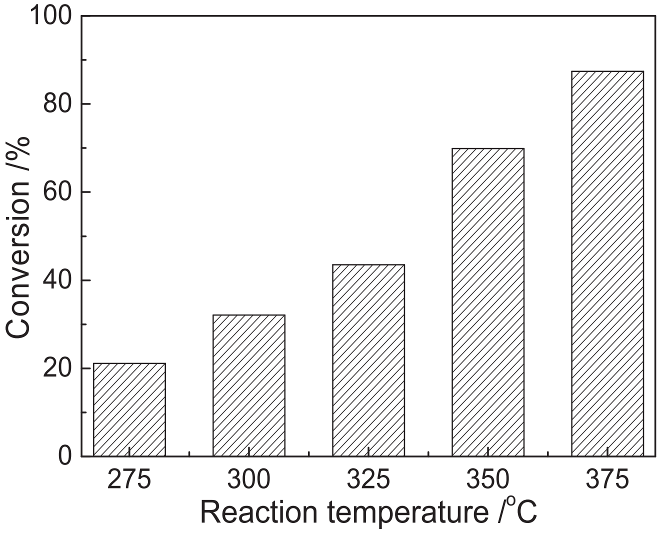
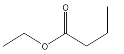
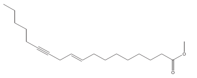
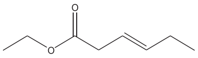
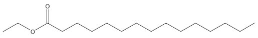
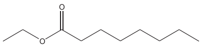
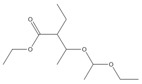
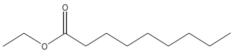
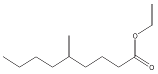
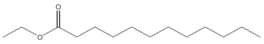
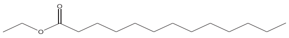
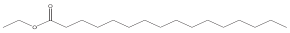
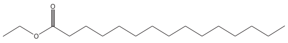
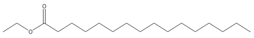
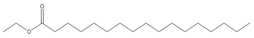
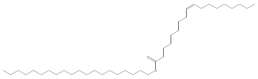
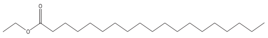
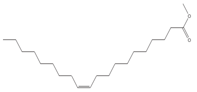
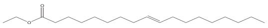
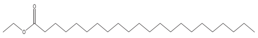
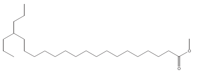
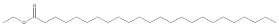
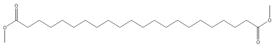
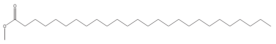


Fig. 1. Conversion of HDK by ethanolysis at different temperatures for 2 h.

are very active and readily undergo further reactions, the second reactions. Due to the interference of the second reactions, it is rarely possible to observe the primary reactions and the primary bond structure. In short, it is imperative and wise to choose a method which can selectively break special bonds to degrade kerogen.

Alcoholysis is an effective strategy to depolymerize complex organic substances through breaking weak bonds (like ether and ester bonds), using low carbon aliphatic alcohols, such as methanol, ethanol, and isopropanol [17,18]. What's more, high extraction yields can be obtained. So far, ethanol has been widely used as a solvent in degrading biomass [19,20] and coal [21,22], by breaking weak bonds to produce quantities of phenols, alcohols, and esters. Much work [21,23,24] has been done to study the mechanism of alcoholysis, showing that depolymerization of coal resulted from the cleavages of weak bonds, like ether bonds, caused by the nucleophilic oxygen atom in ethanol attacks. Li et al. [25] analyzed the ethanol-soluble portion from Zhaotong lignite through supercritical ethanolysis, and obtained a yield of the

Table 2
Esters of ethanolysis products and their mass yields.

No.	Retention time/min	Compounds	Yield/mg per gram of kerogen
1	1.801		11.1
5	3.341		11.4
6	3.47		11.5
12	5.042		11.3
15	7.23		10.9
16	7.412		21.6
17	9.621		10.7
20	12.092		10.8
23	16.831		10.9
26	19.045		10.9
28	21.163		11.1
30	23.18		11.3
32	25.11		22.2
33	26.961		11.7
35	28.641		10.9
36	28.737		12.0
38	30.443		12.3
40	31.994		10.9
41	32.074		13.1
42	33.572		10.9
44	35.096		10.9
45	35.171		12.3
47	36.637		12.1
50	38.054		12.3
51	39.365		11.9
52	39.423		11.6

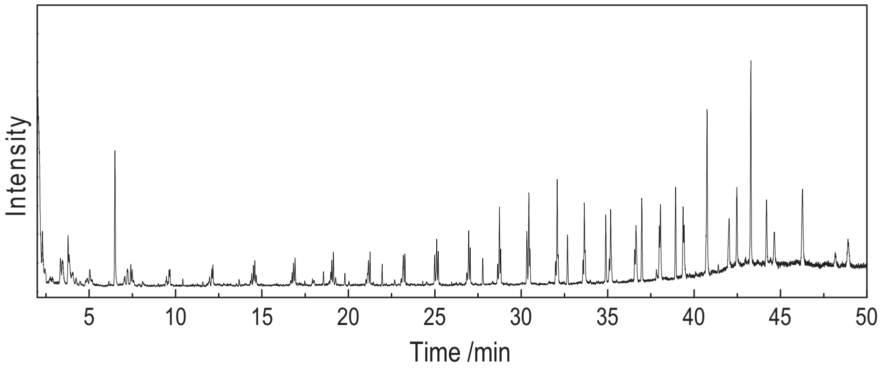


Fig. 2. Total-ion chromatogram (TIC) of the ethanolysis products ES_{375}.