Bioresource Technology 101 (2010) 2860–2866

Contents lists available at ScienceDirect

Bioresource Technology

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

The formation of bio-oil from sludge by deoxy-liquefaction in supercritical ethanol

Li Hui [a,b], Yuan Xingzhong [a,b,*], Zeng Guangming [a,b], Huang Danlian [a,b], Huang Huajun [a,b], Tong Jingyi [a,b], You Qiao [a,b], Zhang Jiachao [a,b], Zhou Ming [c]

[a] *College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China*
[b] *Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha 410082, PR China*
[c] *College of Chemical Engineering and Pharmaceutics, Henan University of Science and Technology, LuoYang 471003, PR China*

ARTICLE INFO

Article history:
Received 6 August 2009
Received in revised form 27 October 2009
Accepted 28 October 2009
Available online 14 December 2009

Keywords:
Deoxy-liquefaction
Ethanol
Bio-oil
GPC
Esterification

ABSTRACT

A novel deoxy-liquefaction of sludge to liquid fuel ($CH_{2.07-1.40}O_{0.30-0.06}N_{0.09-0.05}S_{0.02-0.0032}$) was studied in supercritical ethanol. The reduction of oxygen atoms combined with hydrogen to produce H_2O weaken the reduction of oxygen atoms in the form of CO and CO_2, and the latter process is the primary process for the reduction of oxygen during deoxy-liquefaction. The significant increment of oil and residue fractions yield was obtained in excess ethanol as extraction and polymerization process. The addition of Fe-catalyst could promote the catalytic activity of hydrogenation for free radicals, but inhibited the liquefaction conversion. Esters and acids were identified as main compounds as the decomposing, extraction and esterification process. The conversion of free radicals and intermediates to products with heterocyclics and phenol ring was promoted, and the formation of medium-boiling-point compounds without heterocyclics and phenol ring structure was inhibited at higher temperature and higher solvent filling ratio.

1. Introduction

Sludge is produced as a result of municipal wastewater treatment. The activated sludge production is generally 0.5–1 kg SS per kg BOD_5 removed in the aerobic treatment (Eckenfelder, 2000). Typically, 70% of activated sludge was composed of organic matters, including 32–41% proteins, 5–12% lipids and 15–30% carbohydrates (Pokorna et al., 2009).

The crisis of fuel requires the sustainable development and utilization of fuels. Recently, the recovery of energy from sewage sludge and solid wastes has focused on thermo-chemical processes, such as direct combustion (Otero et al., 2009), gasification (McAuley et al., 2001), pyrolysis (Kim and Parker, 2008; Yang and Jiang, 2009) and liquefaction (Kida et al., 2004; Xu and Lancaster, 2008). Xu and Lancaster (2008) investigated the effects of final temperature, residence time, biomass concentration and catalyst on the liquefaction of secondary pulp/paper sludge in hot-compressed water. The properties of the gas and oil products resulting from the liquefaction operations were also reported. It confirmed that the main contents of secondary pulp/paper sludge were similar to those of lignocellulose, but quite different from those of typical sludge produced from municipal wastewater treatment.

In this study, the effects of final temperature, ethanol/water ratio, solvent filling ratio, and catalyst on the liquefaction of typical sludge in supercritical ethanol were studied. The term of "deoxy-liquefaction" was used to describe the thermal conversion of biomass as deep removal of oxygen during the liquefaction. For the liquefaction of lignocellulose, the process included not only the simple decomposition of biomass but the decrement of the oxygen from biomass with cleavage of the C–O bond. Recently, several researches were investigated on the deoxy-liquefaction of biomass. More than 80% removal of oxygen content were reported in those researches (Guo et al., 2008; Li et al., 2008; Lu et al., 2009; Wang et al., 2008; Wu et al., 2008, 2009). The characteristics of oil and solid products were investigated by elemental, and GC–MS. The objectives of this study are, firstly, to discuss the influence of reaction parameters for the future commercial utilization, and secondly, to present the decomposing and formation routes of the main products during liquefaction process.

2. Experiment

2.1. Materials

The sludge was obtained from an urban wastewater treatment plant in Changsha, Southern China. First, the sludge was dried in an oven at 105 °C for 24 h, and then ground in a rotary cutting mill. The results of chemical analysis are given in Table 1. The higher heating value (HHV) of each valuable fraction is computed from

---

* Corresponding author. Address: College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China. Tel.: +86 73188821413; fax: +86 73188823701.
E-mail address: yxz@hnu.cn (X. Yuan).

0960-8524/$ - see front matter © 2009 Published by Elsevier Ltd.
doi:10.1016/j.biortech.2009.10.084

Table 1
Chemical analysis of sludge, wood and oil.

Sample	Elemental analysis (wt%)					HHV (MJ/kg)	Elemental ratio (mol/mol)				Metal composition[c]			Empirical formula
	C	H	O[a]	N	S		H/C	O/C	N/C	S/C	Zn	Pb	Cd	
Sludge	41.66	5.80	47.52	3.22	1.80	14.57	1.67	0.86	0.07	0.016	1221.5	188.3	6.8	$CH_{1.67}O_{0.86}N_{0.07}S_{0.016}$
Wood[b]	53.30	6.20	40.30	0.10	0.10	19.70	1.40	0.57	0.0016	0.0007				$CH_{1.40}O_{0.57}N_{0.0016}S_{0.0007}$
260 °C	72.73	12.24	9.12	5.17	0.74	40.61	2.02	0.09	0.06	0.0038				$CH_{2.02}O_{0.09}N_{0.06}S_{0.0038}$
280 °C	71.70	12.38	7.96	7.00	0.96	40.67	2.07	0.08	0.08	0.0050	2410	1860	94.7	$CH_{2.07}O_{0.08}N_{0.08}S_{0.0050}$
300 °C	72.26	12.47	7.97	6.35	0.95	41.00	2.07	0.08	0.08	0.0049	1740	370	36.2	$CH_{2.07}O_{0.08}N_{0.08}S_{0.0049}$
320 °C	72.39	11.64	7.81	7.13	1.03	39.87	1.93	0.08	0.09	0.0053				$CH_{1.93}O_{0.08}N_{0.09}S_{0.0053}$
340 °C	73.57	12.48	6.21	6.69	1.05	41.76	2.04	0.06	0.08	0.0054	940	420	21.6	$CH_{2.04}O_{0.06}N_{0.08}S_{0.0054}$
360 °C											912	307	24.1	
380 °C											803	246	12.8	

[a] By difference.

[b] Xu and Etcheverry, (2007).

[c] Obtained at sludge/ethanol 1/40 (g/mL), solvent filling ratio 20 vol%, holding time 10 min, and without catalyst (ppm).

Dulong formula, as follows: HHV (MJ/kg) = 0.3383C + 1.442(H–O/8). It should be noted that it is not accurate to calculate the HHV of sludge with Dulong formula, as some nonflammable substance in sludge. Therefore, the HHV of sludge was analyzed with a calorimeter (KS Auto Calculation Bomb Calorimeter KLSR-4000). Clearly, the HHV of sludge calculated with Dulong formula (13.89 MJ/kg) is nearly similar with that analyzed with the calorimeter (14.57 MJ/kg). Meanwhile, several metals were identified in feedstock, such as Zn (1221.5 ppm), Pb (188.3 ppm), Cd (6.8 ppm), Fe (689.7 ppm), Ca (534.3 ppm), K (217.9 ppm), Al (674.7 ppm), and Mg (188.4 ppm), respectively. The effects of metals on the deoxy-liquefaction of sludge were discussed in this study.

2.2. Experimental procedure and separation

Liquefaction experiments were conducted in a 1000 mL GSHA-1.0 type autoclave at the reaction temperature. The reactants were agitated vertically using stirrer (95 rpm). The temperature was then raised up to the reaction temperature. Afterwards, the autoclave was cooled down to the room temperature by cool water.

Fig. 1 depicts the details of the procedure for separating liquefaction products. After completing the cooling period, the gas product was vented without being further analyzed as very small amount of gas product. The autoclave contents were poured into a beaker (able to be prepared for viscosity analysis). The liquefied products were removed from the autoclave by washing with 150 mL ethanol three times, and then filtered. After removal of ethanol under reduced pressure at 70 °C in a rotary evaporator, liquid phase product was designated as oil. The dark brown solid was dried in an oven at 105 °C overnight, and called as residue. The loss in separation process was named as light fractions. It should be noted that the removal of ethanol in a rotary evaporator is unnecessary in the commercial utilization as the liquid fraction is the potential energy. The objective of removing ethanol in a rotary evaporator is only for quantitative analysis in this research.

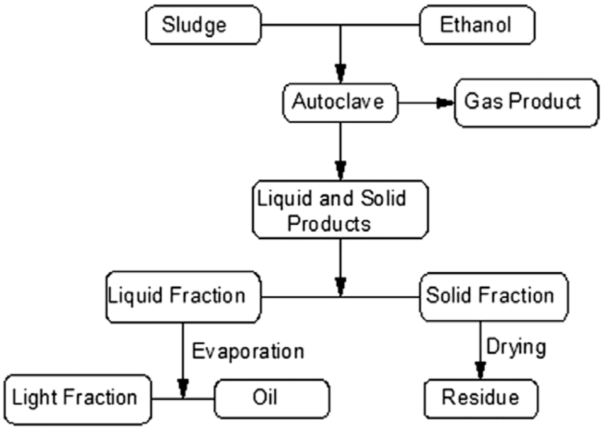

Fig. 1. Procedure for separation of deoxy-liquefaction products.

2.3. Analysis

The element compositions (C, H, O, N, and S) of oil were analyzed by CHNOS Elemental Analyzer Vario EL III (Elementar Analysen systeme GmbH, Germany). Inorganic elements such as Zn, Pb, and Cd were determined using A Perkin–Elmer 700 atomic absorption spectrophotometer, while the concentration of Fe, Ca, K, Al and Mg in feedstock was analyzed by Atomic Absorption Spectroscopy AA-6800 Series Shimadzu. It can be shown from the Table 1 that the elemental composition of sludge is very similar with that of wood, and the HHV of sludge is so low that oxygen needs to be reduced during deoxy-liquefaction process.

The viscosities of liquid fractions were analyzed by KD-R0515 Campaign viscosity meter (Germany Seiko Germany Cadon Instrument Manufacturing Co., Ltd.). GPC analyses were conducted on a PL-GPC120 (Britain Polymer Laboratories).

GC–MS analyses were conducted on a Trace GC, Palaris Q GC–MS spectrometer (Thermo-Finnigan, USA) using carbon capillary column, DB-1 (film thickness, 0.25 mm; column dimensions, 30 m × 0.25 mm), with helium as the carrier gas. The column temperature of GC used in this study was programmed from 130 to 230 °C with an increasing rate of 8 °C/min. The temperature of the injection chamber was 250 °C, and the temperature of transfer line was 230 °C. Mass range was 40–450*m*/*z*.

3. Results and discussion

Batch tests were conducted to investigate the deoxy-liquefaction of the sludge in supercritical ethanol, and hot-compressed ethanol–water mixture. These experiments in pure ethanol runs were performed at temperatures and pressures of 260–400 °C and 7–13 MPa, respectively. These levels are higher than the critical point of ethanol (243 °C, 6.4 MPa).

3.1. Temperature

The yield of residue decreased with final temperature increasing from 260 to 320 °C, and increased with final temperature increasing from 320 to 340 °C (Fig. 2). Meanwhile, the yield of oil increased with the temperature increasing in the range of 280–380 °C. Those were probably due to two reasons.

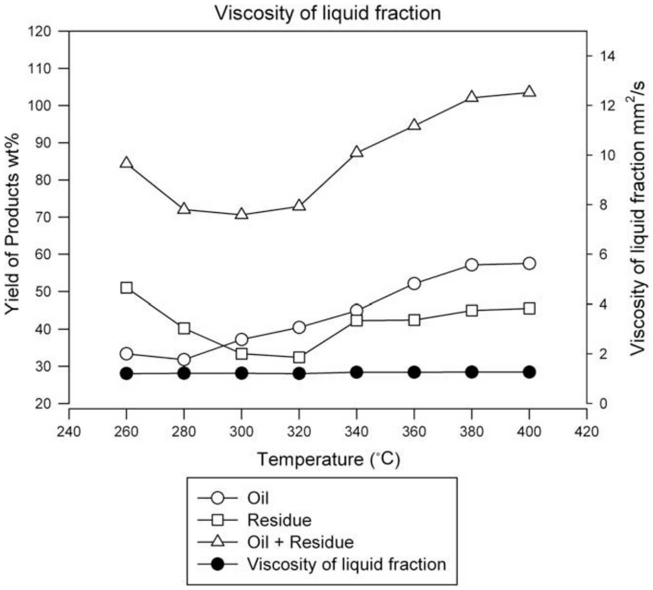

Fig. 2. The yield of products as a function of the temperature at sludge/ethanol 1/40 (g/mL), solvent filling ratio 20 vol%, holding time 10 min, and without catalyst.

First, the decomposing reaction is the main reaction at low temperature, while polymerization reaction is the main reaction at higher temperature. In the range of 260–300 °C, sludge was decomposed in the presence of ethanol, resulting in the decrement of residue yield. In contrast, in the range of 300–400 °C, the polymerization reaction of free radicals (derived from further decomposing of fragment which produced from decomposing of sludge) converting to oil and residue fractions is contributed to the increment of oil and residue yield. This speculation is similar to the mechanism for liquefaction of lignocelluloses in several kinds of solvents, such as wood, rice straw, etc. (Li et al., 2009; Xu and Etcheverry, 2007; Yuan et al., 2009). It showed that decomposing and polymerization reactions were the main reactions at low and high temperature steps in the liquefaction of biomass, respectively.

Second, the conversion of free radicals to residue and oil fractions was promoted in the presence of ethanol, resulting in the increment of oil and residue yields at high temperature. In the range of 320–400 °C, ethanol reacted with the free radicals generated from the decomposing process of sludge to produce the oil and solid products and, consequently, the yields of oil and residue fractions were increased. It can be clearly supported by the yields of oil + residue obtained at 380 and 400 °C, that is, the yields of oil + residue obtained at 380 and 400 °C is higher than 100 wt%.

The oxygen content and O/C ratio of oil (Table 1) were decreased with the temperature increasing in the range of 260–340 °C, leading to a sustaining increment of HHV. According to the previous studies and the results in the present work (Wu et al., 2009; Xu and Etcheverry, 2007; Yuan et al., 2007), the greatly reduced oxygen content in the oil was mainly attributed to two reasons including (1) dehydration reactions as well as formation of CO/CO_2 in the liquefaction process, and (2) a hydrogen-donor process of the combination of oxygen in sludge with hydrogen in ethanol solvent to produce water.

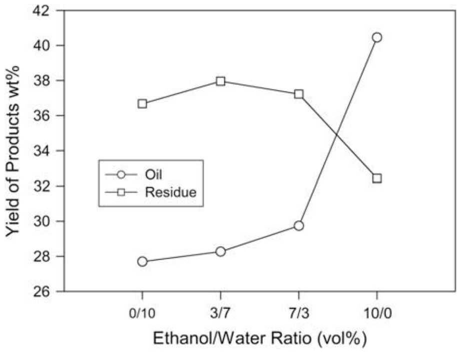

Fig. 3. The yield of products as a function of the ethanol/water ratio at 320 °C, sludge/mixture 1/40 (g/mL), solvent filling ratio 20 vol%, holding time 10 min, and without catalyst.

3.2. Ethanol/water ratio

The effect of ethanol/water ratio on the deoxy-liquefaction yields of oil and sludge is depicted in Fig. 3. The higher the ethanol/water ratio, the higher the yield of oil. The yield of residue increased with the ratio increasing from 0/10 to 3/7 (ethanol/water, v/v), and decreased with the ratio increasing from 3/7 to 10/0. It might be due to the same reason with the mechanism in Section 3.1, that is, the conversion of free radicals to residue and oil fractions was promoted by the presence of ethanol, resulting in the increment of oil and residue yields in pure ethanol runs. However, as the polymerization process at 320 °C was not more active than that at 340 °C, the polymerization at 320 °C might be not more active than hydrogen-donor process, and then the formation of residue (oil) was weakened (promoted) in pure ethanol at 320 °C.

In addition, as reported by a previous research (Wu et al., 2009), the reduction of oxygen atoms in the form of CO and CO_2 was the main process in the liquefaction of biomass in hot-compressed water. The productions of CO and CO_2 increased the amount of gas products, and then CO and CO_2 were the main contents of gas products from liquefaction of biomass in hot-compressed water. In this study, as shown in Table 2, the slight decrement of oxygen contents in oil fractions obtained from the higher ethanol ratios run (7/3 and pure ethanol), presents that deoxy-process was more active in higher ethanol ratios run. The slightly enhanced

Table 2
Effects of ethanol/water and filling solvent ratio on the elemental and thermal analysis of oil.

Sample	Elemental analysis (wt%)					HHV(MJ/kg)	Elemental Ratio (mol/mol)				Empirical formula
	C	H	O[a]	N	S		H/C	O/C	N/C	S/C	
Sludge	41.66	5.8	47.52	3.22	1.8	14.57	1.67	1.95	0.07	0.0037	$CH_{1.67}O_{1.95}N_{0.07}S_{0.016}$
0/10	65.53	10.32	15.36	5.37	3.42	34.28	1.89	0.18	0.07	0.02	$CH_{1.89}O_{0.18}N_{0.07}S_{0.02}$
3/7	57.24	9.83	22.78	7.39	2.76	29.43	2.06	0.30	0.08	0.0049	$CH_{2.06}O_{0.30}N_{0.08}S_{0.0049}$
7/3	69.05	11.39	11.25	5.48	2.83	37.76	1.98	0.12	0.08	0.0053	$CH_{1.98}O_{0.12}N_{0.08}S_{0.0053}$
10/0	72.39	11.64	7.81	7.13	1.03	39.87	1.93	0.08	0.09	0.0054	$CH_{1.93}O_{0.08}N_{0.09}S_{0.0054}$
15 vol%	71.98	10.60	12.01	4.79	0.62	37.47	1.77	0.13	0.06	0.0032	$CH_{1.77}O_{0.13}N_{0.06}S_{0.0032}$
20 vol%	72.39	11.64	7.81	7.13	1.03	39.87	1.93	0.08	0.09	0.0053	$CH_{1.93}O_{0.08}N_{0.09}S_{0.0053}$
25 vol%	71.62	11.58	12.22	3.87	0.71	38.72	1.94	0.13	0.05	0.0037	$CH_{1.94}O_{0.13}N_{0.05}S_{0.0037}$

[a] By difference.

deoxy-process in higher ethanol ratios runs showed that the main deoxy-process in the present study was still CO–CO_2 reduction of oxygen. However, the CO–CO_2 reduction of oxygen was weakened, and the hydrogen-donor reduction of oxygen was promoted as the addition of ethanol. Therefore, the hydrogen-donor reduction of oxygen markedly weakened the CO/CO_2 reduction of oxygen, which resulted in the decrement of gas + light fractions yield and increment of oil yield. This might also explain the reason why the gas products had a too low amount to be analyzed in this study.

3.3. Solvent filling ratio

The effect of solvent filling ratio on the liquefaction process was shown in Fig. 4. The yield of oil obtained at ratio of 25 vol% was higher than those obtained at ratio of 10, 15 and 20 vol%, while the yields of residue obtained at ratio of 10 and 25 vol% were higher than those at the ratio of 15 and 20 vol%. It can be due to that the extraction activity between sludge/free radicals and ethanol was enhanced at ratio of 25 vol%. The increment of solvent filling ratio contributed to the increment of reaction pressure and the density of supercritical ethanol. Therefore, the compounds in the sludge and free radicals obtained from decomposing process were extracted into supercritical ethanol, and then reacted with supercritical ethanol, resulting in the increment of oil products. Meanwhile, the reason for the increment of residue yield in 100 mL run was that the decomposition of sludge was reduced as the lack of solvent, resulting in the increment of residue yield. Second, the polymerization might be enhanced at higher solvent filling ratio, and could be supported by the results of GC–MS. As shown in Table 3, the amount of phenols, naphthalenes, biphenyls, and pyrrolidines obtained at ratio of 25 vol%, 320 °C were higher than those obtained at ratio of 20 vol%, 260–340 °C. The polymerization led to the formation of larger compounds which were transferred into oil and solid fractions during the separation process, resulting in the increment of oil and residue fractions.

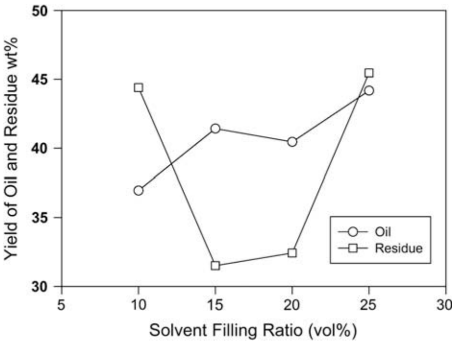

Fig. 4. The yield of products as a function of the solvent filling ratio at 320 °C, sludge/ethanol 1/40 (g/mL), holding time 10 min, and without catalyst.

Table 3
GC–MS analysis of the oil from sludge with supercritical ethanol, in holding time 10 min and sludge 10 g, without catalyst.

Peak	RT	Compound	260 °C[a]	280 °C[a]	320 °C[a]	340 °C[a]	25 vol%
1	4.21	3-Ethyl-5-methyl-pyridine	–	1.48	4.05	6.72	0.78
2	5.40	Tricyclo[4.2.2.0(1,5)]decan-7-ol	–	–	–	0.53	1.08
3	6.63	2-Methyl-benzenemethanol	–	–	0.51	0.85	1.68
4	6.88	Butanedioic acid diethyl ester	0.59	0.80	0.85	–	0.60
5	7.39	Naphthalene	0.55	0.64	0.90	0.64	4.77
6	8.25	Acetic acid, 7-hydroxy-1,3,4,5,6,7-hexahydro-2H-naphthalen-4a-ylmethyl ester	–	–	–	1.25	1.90
7	8.78	2,3,6-Trimethyl-phenol	–	–	–	0.93	2.41
8	9.92	1-(1-Cyclohepten-1-yl)-pyrrolidine	–	–	–	0.50	3.64
9	10.27	2-Methyl-naphthalene	–	–	–	–	2.97
10	10.84	Bezenepropanoic acid ethyl ester	–	–	0.76	0.92	1.14
11	11.80	Biphenyl	–	–	–	–	1.88
12	12.14	5,7-Dodecadiyn-1,12-bis(carbamic acid butyloxymethyl ester)	–	–	0.61	0.87	–
13	12.24	2-Ethyl- naphthalene	–	–	–	–	3.30
14	12.66	2,3-Dihydro-3,3-dimethyl-1H-inden-1-one	–	–	–	–	0.56
15	12.90	2,5-Bis(1-methylethyl)-phenol	–	–	–	–	1.11
16	14.28	[1-(2,4-Cyclopentadien-1-ylidene)ethyl]-benzene	–	–	–	–	0.56
17	14.49	2-Methyl-1,1′-biphenyl	–	–	–	–	1.05
18	16.76	Pentadocanoic acid	1.24	1.29	1.02	0.96	0.74
19	17.90	1,4-Benzenedicarboxylic acid diethyl ester	0.49	0.81	–	–	–
20	21.08	*n*-Hexadecanoic acid	4.07	3.73	3.24	2.95	2.22
21	21.83	13-Heptadecyn-1-ol	0.50	0.56	–	–	–
22	22.33	Nonanedioic acid dibutyl ester	1.84	2.09	1.60	1.48	1.01
23	22.50	Heptadecanoic acid	1.42	1.66	1.22	1.10	0.76
24	23.06	Nonanedioic acid bis(2-methylpropyl) ester	1.39	1.34	1.38	1.50	0.80
25	24.56	Ethyl 9-hexadecenoate	5.04	4.13	4.25	1.74	2.65
26	25.18	Octadecanoic acid	32.44	11.35	29.72	27.88	13.51
27	26.18	*n*-Heptadocanoic-14-methyl-methyl ester	–	0.68	0.50	–	–
28	26.85	Octadecanoic acid methyl ester	0.93	1.34	0.90	0.90	0.89
29	27.95	9,12-Octadecadienoic acid (Z,Z)-2,3-dihydroxypropyl ester	2.05	0.86	0.82	–	0.85
30	28.15	Ethyl oleate	6.12	4.08	5.79	3.93	4.65
31	28.27	9-Octadecanoic acid (Z)-2-hydroxy-1-(hydroxymethyl)ethyl ester	8.48	8.44	8.16	7.37	5.11
32	28.67	Heptadocanoic acid 15-methyl-ethyl ester	10.82	16.59	10.72	9.44	7.66
33	29.49	Linoleic acid ethyl ester	0.62	2.11	0.51	0.71	–
34	31.41	11-Eicosenoic acid methyl ester	0.67	1.47	0.53	–	0.51
35	31.87	Heneicosanoic acid methyl ester	1.29	1.04	1.09	1.05	0.85
36	34.54	Erucic acid	1.05	2.71	0.77	0.53	0.75
37	35.00	Tricosanoic acid methyl ester	1.10	2.32	0.82	0.74	0.81
38	40.14	$C_{27}H_{46}$	0.79	1.68	0.64	0.51	0.42
39	40.73	(5a)-Cholest-7-ene	0.62	1.68	0.67	0.67	0.46
Total			86.81	77.48	85.67	81.51	76.72

[a] 200 ml (20 vol%) ethanol.

In addition, the mechanism for the effect of solvent filling ratio on the liquefaction process was supported by the elemental analysis (Table 2). The oxygen content in 200 mL (20 vol%) run was lower than those in 150 (15 vol%) and 250 mL (25 vol%), identifying the halfway decomposition (10 vol% run) and active reaction (25 vol% run) occur, respectively.

3.4. Catalyst

As shown in Fig. 5, the yields of oil and residue in Fe-catalyst runs were mostly higher than those in alkaline and non-catalyst runs. It was considered due to that Fe-catalysts can improve the hydrogen transfer from hydrogen-donor solvent and/or sludge to the fragments derived from decomposing of sludge, leading to stabilization of those fragments. Therefore, the yields of oil and solid fractions were increased. The improved hydrogenation was also identified by results of elemental analysis. In Table 4, H and H/C in oil in Fe-catalyst runs were slightly higher than the other runs. It was found that the sulphur in the sludge improved the catalytic activity of hydrogenation in this study, which accorded with the observation reported by other researchers (Wang et al., 2007). The lowest yield of residue of 31.33 wt% in K_2CO_3 run indicated that the higher yields of oil and gas + light fractions obtained from the liquefaction process (Karagoz et al., 2005). However, compared with the residue yield of 32.43 wt% in no-catalyst run, the addition of K_2CO_3 to liquefaction process can only contribute to the decrement of 1.1 wt% for residue yield. In other words, the addition of catalyst can not markedly increase the liquefaction conversion of feedstock in this study. The addition of Fe-catalyst to the liquefaction has a capability to promote the hydrogenation process of free radicals, but decrease the liquefaction conversion of feedstock (100 wt%-residue yield wt%).

In addition, specific metals in the sludge also could catalyze the deoxy-liquefaction of sludge, i.e., Ni catalyzed the decomposition of methane, Cr, Cu, Fe or Zn catalyzed the water–gas shift reaction, alkaline earth metal catalyzed the formation of water-soluble oil, and Ca enhanced organic conversion (Domínguez et al., 2008; Xu and Lancaster, 2008). Therefore, the addition of catalyst cannot markedly increase the liquefaction conversion of feedstock in this study.

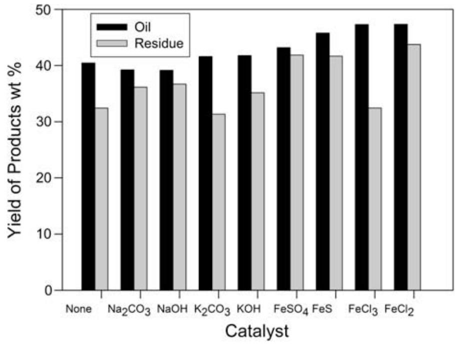

Fig. 5. The yield of products as a function of catalyst at 320 °C, sludge/ethanol 1/40 (g/mL), solvent filling ratio 20 vol%, and holding time 10 min.

3.5. Viscosity analysis

The viscosities of liquid fractions were shown in Fig. 2. The viscosities of liquid fractions were in the range of 1.21–1.27 mm/s. Compared with the viscosities of gasoline, diesel oil and biodiesel, the order of fuel viscosities can be ranked as follows: gasoline < liquid fraction in this study < diesel oil < biodiesel.

3.6. Elemental analysis

Compared with the elemental composition of the crude sludge powder (Table 1), the obtained oil fraction in mixture and pure ethanol runs contained higher concentrations of carbon (71.62–73.57 wt%), hydrogen (10.60–12.48 wt%) and nitrogen (3.87–7.46 wt%). The empirical formula of $CH_{2.07-1.40}O_{0.30-0.06}N_{0.09-0.05}S_{0.02-0.0032}$ for oils was contrary to $CH_{1.67}O_{0.86}N_{0.07}S_{0.016}$ for sludge (Table 1). The lower O/C ratios and oxygen content in oil fractions might be attributed to the hydrogenation reactions in the supercritical ethanol system due to the special roles of supercritical ethanol in the liquefaction process as explained in Section 3.2. Furthermore, the hydrogen content and H/C ratio in oil fractions of this research were higher than those in feedstock, which is likely due to the hydrogenation of supercritical ethanol in the liquefaction process. Nevertheless, the hydrogenation does not affect the change of nitrogen atom during the liquefaction process, and the removal of nitrogen atom was not identified from experiment results.

Previous researchers reported that the H/C of oil fractions were lower than those of feedstock during liquefaction of biomass (lignocelluloses and secondary pulp/paper sludge powder) in hot-compressed water, hydrogen-donor solvents and mixed solvents (Li et al., 2009; Xu and Etcheverry, 2007; Xu and Lancaster, 2008; Yuan et al., 2007). However, comparing with previous results, the H/C ratios of oil fractions were promoted, while O/C ratio in oil fractions were reduced in the present study. This diversity could be explained by the different structure between sludge and lingocellulose. Among the three components of biomass, lignin was the most difficult one to decompose, and lignin occurs mostly as lignocellulose in complex association with cellulose in biomass (Demirbas, 2000). However, the sewage sludge appears more reactive, suggesting different molecular structures, perhaps involving a greater degree of bonding through thermally labile O– and S–ether bridges. The distinctive structural characteristic of lignocellulose make them resistant to attack by hydrogen free radical (H$^\cdot$) from the hydrogen-donor solvent, and then the hydrogenation process was enhanced in the liquefaction of sludge in supercritical ethanol.

Table 4
Effect of catalyst on the elemental and thermal analysis of oil.

Sample	Elemental analysis (wt%)					HHV(MJ/kg)	Elemental ratio (mol/mol)				Empirical formula
	C	H	O[a]	N	S		H/C	O/C	N/C	S/C	
None	72.39	11.64	7.81	7.13	1.03	39.87	1.93	0.08	0.09	0.0053	$CH_{1.93}O_{0.08}N_{0.09}S_{0.0053}$
Na_2CO_3	72.92	10.97	8.70	6.73	0.68	38.71	1.81	0.09	0.08	0.0035	$CH_{1.93}O_{0.08}N_{0.09}S_{0.0053}$
NaOH	71.93	11.62	8.79	7.02	0.64	39.51	1.94	0.09	0.08	0.0033	$CH_{1.94}O_{0.13}N_{0.05}S_{0.0037}$
$FeSO_4$	72.29	12.37	6.94	7.46	0.94	41.04	2.05	0.07	0.09	0.0049	$CH_{2.05}O_{0.07}N_{0.09}S_{0.0049}$
FeS	71.65	11.90	8.18	7.40	0.87	39.92	1.99	0.09	0.09	0.0046	$CH_{1.99}O_{0.09}N_{0.09}S_{0.0046}$

[a] By difference.

3.7. GC–MS analysis

To investigate the effect of temperature and solvent filling ratio on the type of the compounds in the oil products, the oil fractions obtained at different reaction temperatures (260, 280, 320 and 340 °C) were analyzed by GC–MS. Table 3 lists the tentative compounds of the oil and PA + A fractions, which are the most probable compounds identified by the MS search file (NIST library). Meanwhile, the oil from sludge with supercritical ethanol, at temperature (280, 320 and 340 °C) holding time 10 min and sludge 10 g, without catalyst were analyzed by GPC. The GPC analysis (not shown) is shown that the molecular weights of more than 85 wt% of compounds in oil fractions are smaller than 400, and can be suitable in GC–MS.

As shown in Table 3, four esters and two acids were identified as main compounds in different temperature, solvent filling ratio, and catalyst, respectively, such as *n*-hexadecanoic acid (RT 21.08), ethyl 9-hexadecenoate (RT 24.56), octadecanoic acid (RT 25.18), 9-octadecanoic acid (Z)-2-hydroxy-1-(hydroxyl-methyl)ethyl ester (RT 28.27), heptadocanoic acid 15-methyl-ethyl ester (RT 28.67). *n*-hexadecanoic and octadecanoic acid was observed from GC–MS with a low amount in liquefaction of lignocelluloses (Karagoz et al., 2004, 2005; Li et al., 2009; Wang et al., 2008; Zhang et al., 2007), but with a high amount in liquefaction of secondary pulp/paper sludge (Xu and Lancaster, 2008). Acids might be produced from the decomposing of protein, and the biochemical process for the formation of sludge increased the amount of proteins in the feedstock.

As can be seen in Table 3, the categories and abundance of products with lower (retention time less than 15 min) and medium (retention time less than 29 min) boiling points were greatly affected by the temperature and solvent filling ratio. For the lower boiling points products, the higher amount of heterocyclics (RT 4.21: 3-ethyl-5-methyl-pyridine), esters (RT 8.25: Acetic acid, 7-hydroxy-1,3,4,5,6,7-hexahydro-2H-naphthalen-4a-ylmethyl ester), phenol derivatives (RT 8.78: 2,3,6-trimethyl-phenol) were obtained at higher final temperature (340 °C), while the higher amount of heterocyclics (RT 9.92:1-(1-cyclohepten-1-yl)-pyrrolidine), biphenyl (RT 11.80: biphenyl; RT 14.49: 2-methyl-1,1′-biphenyl), esters, phenol (RT 8.78: 2,3,6-trimethyl-phenol; RT 12.90: 2,5-bis(1-methylethyl)-phenol) derivatives, and alcohols (RT 6.63: 2-methyl-benzenemethanol) were obtained at higher solvent filling ratios (25 vol%). Those compounds almost have structure of heterocyclics and phenol ring. Meanwhile, for the medium boiling points products, the lower amount of acid (RT 21.08: *n*-hexadecanoic acid; RT 22.50: heptadecanoic acid; RT 24.56: ethyl 9-hexadecenoate; RT 25.18: octadecanoic acid), ester (RT 22.35: nonanedioic acid, dibutyl ester; RT 27.95: 9,12-octadecadienoic acid (Z, Z)-2,3-dihydroxypropyl ester; RT 28.27: 9-octadecanoic acid (Z)-2-hydroxy-1-(hydroxymethyl)ethyl ester; RT 28.67: heptadocanoic acid 15-methyl-ethyl ester) were obtained at higher final temperature (340 °C) or higher solvent filling ratios (25 vol%). Those compounds almost have no structure of heterocyclics and phenol ring. Therefore, the conversion of free radical and intermediate to products with heterocyclics and phenol ring were promoted, and the formation of medium-boiling-point compounds without heterocyclics and phenol ring structure (such as acid, ester, etc.) was inhibited at higher temperature and higher solvent filling ratio. In contrast to the trend of heterocyclics yield for final temperature, the formation of heterocyclics from liquefaction process of lignocellulose was inhibited at higher temperature (Liu and Zhang, 2008). The difference of structure and component between sludge and biomass can contribute to that distinction. This oil contained nitrogen derived from protein in the sewage sludge. This nitrogen was in the form of pyridine and pyrrolidine, and needed to be removed from the oil before use (Inoue et al., 1997).

Generally, the acid derivatives formed during the decomposing and extraction process of sludge, while the ester derivatives formed during the extraction and esterification process in supercritical ethanol. The components in the sludge feedstock were decomposed at the starting stage of liquefaction, and then to produce acid derivatives. The presence of supercritical ethanol could promote the formation of esters derivatives during esterification process. The acid and ester derivatives almost have the structure of larger molecular weight with medium boiling point (retention time: 20–29 min). However, the decomposing of acid and ester derivatives to smaller radicals was promoted, and then the repolymerization of smaller radicals occurred at higher temperature. Meanwhile, the free radicals from primary and decomposing process would react with supercritical ethanol which is a hydrogen-donor solvent via some reactions to produce compounds with heterocyclics and phenol ring. After those reactions, the ethanol soluble products enhanced the yield of oil fractions, while the ethanol insoluble (residue) enhanced the yield of residue fractions. Those speculations could indicate another reason for the increment of oil and residue fractions yield at solvent filling ratio of 25 vol% in Section 3.3.

3.8. Metal analysis

The amounts of Zn, Cd, and Pb in oil fractions obtained at 280, 300, 340, 360 and 380 °C with sludge/ethanol 1/40 (g/mL), solvent filling ratio 20 vol%, holding time 10 min, and without catalyst were shown in Table 1. The concentrations of those metals increased during the liquefaction process, and the highest amounts of metals were obtained at lower temperature. Those results were obviously different from the research results on the pyrolysis of sludge that the heavy metals were concentrated in residue fractions during pyrolysis (Caballero et al., 1997). That diversity should be responsible for the decomposing and extraction capabilities of ethanol in the supercritical liquefaction process, and then the heavy metals were dissolved in the liquid fractions. Meanwhile, at higher temperature, the formation of solid products made the heavy metals into solid fractions and, consequently, the amounts of heavy metals in oil fractions at higher temperature were lower than those at lower temperature.

It is necessary for the removal of heavy metals, which was outside the scope of this work, to meet the requirement for commercial utilization in the future as the enhanced amounts of heavy metals in liquid fractions in the liquefaction process.

4. Conclusion

In the two reactions for the reduction of oxygen during the deoxy-liquefaction of sludge, the form of CO and CO_2 was the main process. The reactions of compounds in the sludge and free radicals with supercritical ethanol were promoted at higher ratio. The addition of Fe-catalyst promoted the catalytic activity of hydrogenation for free radicals, but decreased the liquefaction conversion. The conversions of free radical and intermediate to products with heterocyclics and phenol ring were enhanced, and the formation of medium-boiling-point compounds without heterocyclics and phenol ring structure was inhibited at higher temperature and higher solvent filling ratio.

Acknowledgements

This research was financially supported by the National Natural Science Foundation of China (No. 50678062), the National Basic Research Program of China (2005CB724203), Chinese National Natural Foundation for Distinguished Young Scholars Project (No.

50225926), the Program for Changjiang Scholars, and Innovative Research Team in University (IRT0719) and Key Project for Science and Technology Research, Ministry of Education (No. 108100).

References

Caballero, J.A., Front, R., Marcilla, A., Conesa, J.A., 1997. Characterization of sewage sludges by primary and secondary pyrolysis. J. Anal. Appl. Pyrol. 40–41, 433–450.

Demirbas, A., 2000. Mechanisms of liquefaction and pyrolysis reactions of biomass. Energy Convers. Manage. 41, 633–646.

Domínguez, A., Fernández, A., Fidalgo, B., Pis, J.J., Menéndez, J.A., 2008. Bio-syngas production with low concentrations of CO_2 and CH_4 from microwave-induced pyrolysis of wet and dried sewage sludge. Chemosphere 70, 397–403.

Eckenfelder, W.W., 2000. Industrial Water Pollution Control. McGraw-Hill, Boston.

Guo, S.P., Wu, L.B., Wang, C., Li, J.H., Yang, Z.Y., 2008. Direct conversion of sunflower shells to alkanes and aromatic compounds. Energy Fuel 22, 3517–3522.

Inoue, S., Sawayama, S., Dote, Y., Ogi, T., 1997. Behaviour of nitrogen during liquefaction on dewatered sewage sludge. Biomass Bioenergy 12, 473–475.

Karagoz, S., Bhaskar, T., Muto, A., Sakata, Y., 2004. Effect of Rb and Cs carbonates for production of phenols from liquefaction of wood biomass. Fuel 83, 2293–2299.

Karagoz, S., Bhaskar, T., Muto, A., Sakata, Y., Oshiki, T., Kishimoto, T., 2005. Low-temperature catalytic hydrothermal treatment of wood biomass: analysis of liquid products. Chem. Eng. J. 108, 127–137.

Kida, T., Guan, G.P., Yamada, N., Ma, T.L., Kimura, K., Yoshida, A., 2004. Hydrogen production from sewage sludge solubilized in hot-compressed water using photo-catalyst under light irradiation. Int. J. Hydrogen Energy 29, 269–274.

Kim, Y., Parker, W., 2008. A technical and economic evaluation of the pyrolysis of sewage sludge for the production of bio-oil. Bioresource Technol. 99, 1409–1416.

Li, J.H., Wu, L.B., Yang, Z.Y., 2008. Analysis and upgrading of bio-petroleum from biomass by direct deoxy-liquefaction. J. Anal. Appl. Pyrol. 81, 199–204.

Li, H., Yuan, X.Z., Zeng, G.M., Tong, J.Y., Yan, Y., Cao, H.T., Wang, L.H., Cheng, M.Y., Zhang, J.C., Yang, D., 2009. Liquefaction of rice straw in sub- and supercritical 1,4-dioxane–water mixture. Fuel Process Technol. 90, 657–663.

Liu, Z., Zhang, F.S., 2008. Effects of various solvents on the liquefaction of biomass to produce fuels and chemical feedstocks. Energy Convers. Manage. 49, 3498–3504.

Lu, W.P., Wang, C., Yang, Z.Y., 2009. The preparation of High caloric fuel (HCF) from water hyacinth by deoxy-liquefaction. Bioresource Technol. 100, 6451–6456.

McAuley, B., Kunkel, J., Manahan, S.E., 2001. A new process for the drying and gasification of sewage sludge. Water Eng. Manage. 148, 18–20.

Otero, M., Calvo, L.F., Gil, M.V., García, A.I., Morán, A., 2009. Co-combustion of different sewage sludge and coal: a non-isothermal thermogravimetric kinetic analysis. Bioresource Technol. 99, 6311–6319.

Pokorna, E., Postelmans, N., Jenicek, P., Schreurs, S., Carleer, R., Yperman, J., 2009. Study of bio-oils and solids from flash pyrolysis of sewage sludges. Fuel 88, 1344–1350.

Wang, Z.C., Shui, H.F., Zhang, D.Y., Gao, J.S., 2007. A Comparison of FeS, FeS + S and solid superacid catalytic properties for coal hydro-liquefaction. Fuel 86, 835–842.

Wang, C., Pan, J.X., Li, J.H., Yang, Z.Y., 2008. Comparative studies of products produced from four different biomass samples via deoxy-liquefaction. Bioresource Technol. 99, 2778–2786.

Wu, L.B., Guo, S.P., Wang, C., Yang, Z.Y., 2008. Direct deoxy-liquefaction of poplar leaves to biopetroleum with two kinds of catalysts. Ind. Eng. Chem. Res. 47, 9248–9255.

Wu, L.B., Guo, S.P., Wang, C., Yang, Z.Y., 2009. Production of alkanes (C_7–C_{29}) from different part of poplar tree via direct deoxy-liquefaction. Bioresource Technol. 100, 2069–2076.

Xu, C.B., Etcheverry, T., 2007. Hydro-liquefaction of woody biomass in sub- and super-critical ethanol with iron-based catalysts. Fuel 87, 335–345.

Xu, C.B., Lancaster, J., 2008. Conversion of secondary pulp/paper sludge powder to liquid oil products for energy recovery by direct liquefaction in hot-compressed water. Water Res. 42, 1571–1582.

Yang, X.Y., Jiang, Z.P., 2009. Kinetic studies of overlapping pyrolysis reactions in industrial waste activated sludge. Bioresource Technol. 100, 3663–3668.

Yuan, X.Z., Li, H., Zeng, G.M., Tong, J.Y., Xie, W., 2007. Sub- and supercritical liquefaction of rice straw in the presence of ethanol–water and 2-propanol–water mixture. Energy 32, 2081–2088.

Yuan, X.Z., Tong, J.Y., Zeng, G.M., Li, H., Xie, W., 2009. Comparative studies of products obtained at different temperatures during straw liquefaction by hot compressed water. Energy Fuel 23, 3262–3267.

Zhang, T., Zhou, Y.J., Liu, D.H., Petrus, L., 2007. Qualitative analysis of products formed during the acid catalyzed liquefaction of bagasse in ethylene glycol. Bioresource Technol., 1454–1459.