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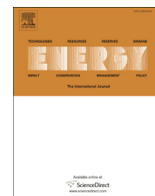**42** PUBLICATIONS **614** CITATIONS

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Comparative studies of thermochemical liquefaction characteristics of microalgae, lignocellulosic biomass and sewage sludge

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ABSTRACT

Lignocellulosic biomass, microalgae and sewage sludge have distinct compositions and structures to each other. To understand the effect of feedstock differences on biomass liquefaction process, the liquefaction characteristics of rice straw (lignocellulosic biomass), *Spirulina* (microalgae) and sewage sludge were comparatively studied. Liquefaction experiments were performed in a 500 mL autoclave at identical conditions (623 K, 9.4–10.1 MPa and 20 min retention time). Although the content of organic materials in sewage sludge was the lowest among above three biomasses, the yield of bio-oil from sewage sludge reached up to 39.5 ± 1.16%, higher than those from rice straw (21.1 ± 0.93%) and *Spirulina* (34.5 ± 1.31%). Besides, the bio-oils from sewage sludge had the highest heating value (36.14 MJ/kg). However, *Spirulina* showed the highest conversion (79.7 ± 1.02%). GC–MS analysis results indicated that the major compounds in the bio-oil from rice straw were phenolic compounds. In case of sewage sludge and *Spirulina*, esters were the main compositions. The volatility distribution of hydrocarbons was evaluated by C-NPgram (Carbon-Normal Paraffin gram). It was showed that the majority of hydrocarbons from sewage sludge and *Spirulina* were distributed at C_{17} and C_{20}, whereas they were distributed at C_8 in rice straw-derived bio-oil. The types of feedstocks have a significant effect on biomass liquefaction.

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1. Introduction

Renewable energy has generated much interest due to the energy crisis, the rising oil prices, the green house effect, and political factors [1]. Biomass is one of the most abundant sources of renewable energy, and will be an important part of a more sustainable future energy system [2]. Biomass resources include wood and wood waste, energy crops, aquatic plants, agricultural crops, and animal wastes. Municipal and milling activities generate huge quantities of mixed biomass like sawdust, manure, sewage sludge and cooking wastes [3]. Biomass is a broad definition and includes a wide range of materials with varying compositions. The main biomass components are: carbohydrates, lignin, protein and lipids [2].

Conversion of biomass to energy is undertaken using two main process technologies: thermo-chemical and bio-chemical/biological [2]. Within thermo-chemical conversion, four process options are available: direct combustion, pyrolysis, gasification and liquefaction. Liquefaction is a low temperature and high pressure thermochemical process during which biomass is broken down into fragments of small molecules in water or another suitable solvent. These light fragments, which are unstable and reactive, can then re-polymerize into oily compounds with various ranges of molecular weights [4]. In recent years, liquefaction has been demonstrated with or without the presence of catalysts for a range of biomasses including lignocellulosic biomass [5–7], microalgae [8–10], sewage sludge [11–14] and so on.

Lignocellulosic biomass materials are the most widely used types of biomass for bio-oil production through liquefaction [4]. The main components of lignocellulosic biomass are cellulose, hemicellulose, and lignin [15]. Microalgal biomass has been recognized as attractive feedstock for the third generation biofuel [9]. Microalgae, a ubiquitous eukaryotic microorganism, can be rich in proteins or rich in lipids or have a balanced composition of lipids, sugars and proteins [16,17]. Sewage sludge produced in municipal wastewater treatment plants is composed mainly of bacterial

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constituents (nucleic acids, proteins, carbohydrates and lipids) and their decay products, undigested organic material (cellulose) and inorganic material [18]. In a word, above three biomasses have distinct compositions and structures to each other.

Biomass liquefaction product is determined by various factors, including substrate type, heating conditions, solvent type, reactor configuration and catalyst [19]. In particular, the type of substrate has remarkable effect on the liquefaction reaction. Specifically, the yields and chemical characteristics of bio-oils can be influenced by the ratio of protein, lipid, and carbohydrate fractions in the initial biomass feedstock [12]. Many papers have been published on the liquefaction of lignocellulosic biomass, microalgae and sewage sludge [5–14]. However, these investigations cannot be compared due to the difference in the separation of products and definition of the liquid product. To the best of our knowledge, there are no studies carried out at identical conditions to understand the effect of distinct compositions and structures among lignocellulosic biomass, microalgae and sewage sludge on the distributions and properties of liquefaction products.

To enhance the bio-oil yield with lower oxygen content, organic solvents, such as ethanol, methanol, acetone, etc., have been utilized as the reaction medium instead of water in recent years [9,10,20]. Among these organic solvents, ethanol may be the most promising solvent for biomass liquefaction from the viewpoint of efficiency, environmental friendliness and reproducible ability. Ethanol has several advantages: First, the critical temperature and critical pressure of ethanol (516.2 K, 6.38 MPa) are far below those of water, so much milder reaction conditions can be obtained. Second, ethanol can provide active hydrogen as a hydrogen-donor in the liquefaction process. Third, ethanol can react with acidic components in the bio-oil by esterification reaction to obtain fatty acid ethyl esters similar to biodiesel. Finally, due to its relatively lower dielectric constant, ethanol can readily dissolve relatively high-molecular weight products derived from biomass [21,22].

In the present work, rice straw (lignocellulosic biomass), *Spirulina* (microalgae) and sewage sludge were chosen as the liquefaction feedstocks and ethanol was adopted as the liquefaction solvent. All the liquefaction experiments were conducted in a same autoclave at identical conditions. The distributions of liquefaction products and bio-oil compositions were comparatively studied.

2. Experimental

2.1. Materials

Dewatered sewage sludge (SS) was obtained from a sewage treatment plant in Changsha City, Hunan Province. Microalgae cells of *Spirulina* (SP) were provided by Xigema Biological Technology Co., Ltd. (Fujian, China). Rice straw (RS) was collected from a farm in the suburbs of Changsha City. Sun dried samples, separated from physical impurities, were ground in a rotary cutting mill and were screened into fractions of particle diameter (d_p) between 0.2 and 0.9 mm. Then the powder was dried in an oven at 378 K for 24 h before use. The solvents used were analytical reagent grade ethanol and acetone. All chemicals were used without further treatment.

The moisture content of biomass samples was determined by drying method (378 K for 24 h). The amounts of combustibles and ash in biomass samples were analyzed by burning them at 873 K for 30 min. And the elemental compositions were analyzed by a CHNOS elemental analyzer (Vario EL III, Germany). The proximate and ultimate analysis results of biomass samples are given in Table 1. The crude protein content in sewage sludge and *Spirulina* were determined by combustion method (AOAC 990.03). Crude lipid was measured gravimetrically after ether solvent extraction (AOAC 945.16). Total carbohydrates were calculated using the

Table 1
Physicochemical characteristics of feedstocks.

Samples	Sewage sludge (SS)	Rice straw (RS)	*Spirulina* (SP)
Proximate analysis (wt.%)			
Moisture	5.6	7.6	3.3
Combustibles[a,b]	60.8	88.3	91.4
Ash[a]	39.2	11.7	8.6
Elemental analysis (wt.%)[c]			
C	43.38	45.04	43.17
H	5.91	5.05	8.53
N	3.18	1.06	8.91
O[d]	47.53	48.85	39.39
H/C (n.d.)[e]	1.63	1.35	2.37
O/C (n.d.)	0.82	0.81	0.68
Caloric value (MJ/kg)[f]	14.63	13.71	19.80

[a] On a dry basis.
[b] Including volatile matter and fixed carbon.
[c] On a dry and ash free basis.
[d] Calculated by difference and assuming that the sulfur content is negligible.
[e] Non dimension.
[f] Higher heating value (HHV).

equation: total carbohydrates (wt.%) = combustibles (wt.%) − (crude protein + crude lipid) (wt.%) [12]. The content of lignin, cellulose and hemicellulose in rice straw were analyzed by a full-automatic fiber analysis system (Foss Fibertec 2010, Sweden). The composition analysis results of each feedstock are presented in Table 2.

2.2. Liquefaction apparatus and procedure

Hydrothermal liquefaction experiments have been carried out in a bath stainless steel autoclave reactor (GSHA-0.5) equipped with a magnetic stirrer (Fig. 1). The reactor was obtained from Xintai Chemical Machinery Co., Ltd. (Weihai, China) with a volume capacity of 500 mL and designed to a maximum temperature and pressure of 723 K and 30 MPa, respectively. Samples were converted into bio-oil under identical conditions (623 K, 9.4–10.1 MPa, and 20 min retention time) in single runs for each feedstock. The focus of this paper was on studying the effect of feedstock type on the distributions and properties of liquefaction products. The influence of liquefaction parameters, e.g. reaction temperature, residence time, solid-to-liquid ratio and so on, was just beyond the scope of this study. Therefore, fixed liquefaction experiment conditions were chosen.

In a typical run, 7.8954 g of dried feedstock and 100 mL of ethanol were loaded into the reactor vessel which was then sealed. Electric resistance heating was then used to raise the temperature to 623 K and the feedstock was continuously mixed by a magnetic drive agitator. The temperature inside the reactor was monitored

Table 2
Composition analysis of feedstocks.

Component analysis (wt.%)[a]	SS	RS	SP
Crude protein	33.6	–[c]	63.4
Crude lipid	6.9	–	7.5
Total carbohydrates[b]	20.3	–	20.5
Lignin	–	9.2	–
Cellulose	–	41.3	–
Hemicellulose	–	24.6	–

[a] On a dry solid basis.
[b] Calculated by subtraction.
[c] Not measured.
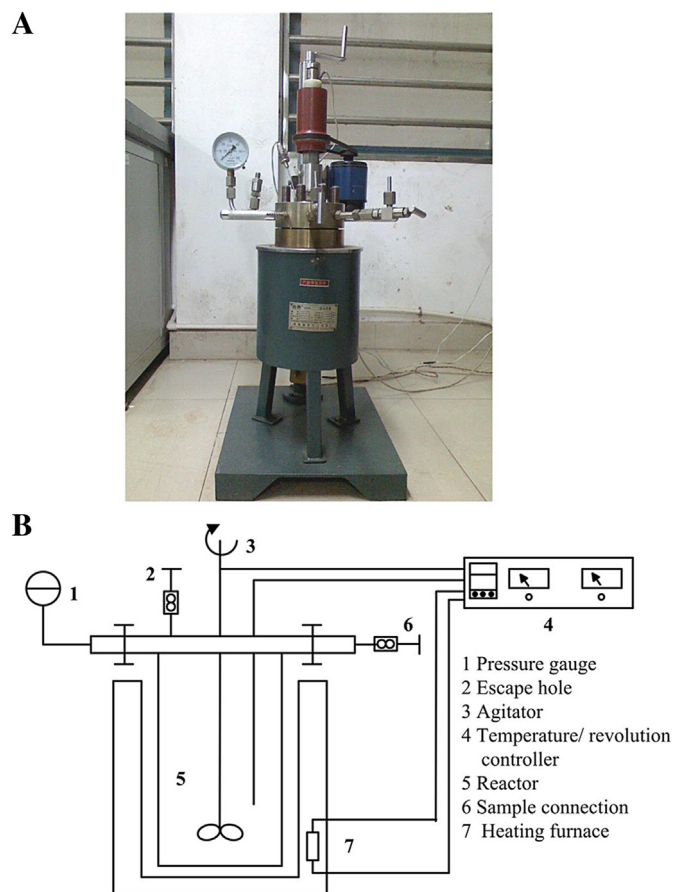
Fig. 1. Experimental apparatus used for liquefaction (A: Vessel picture; B: Schematic diagram).

1 Pressure gauge
2 Escape hole
3 Agitator
4 Temperature/ revolution controller
5 Reactor
6 Sample connection
7 Heating furnace

Fig. 2. Procedure for separation of liquefaction products.

using an inner thermocouple and controlled by a proportional integral derivative module. After a 20-min reaction time, the reactor was cooled rapidly to room temperature by circulating water through a cooling coil located inside the reactor. Heating time is about 50—60 min and 1 h will be taken to cool the reactor to room temperature.

2.3. Separation procedure

The procedure for the separation of liquefaction products is shown in Fig. 2. Now that the dominant species in the gaseous products is CO_2, the gaseous products were not collected and analyzed [13,23,24]. Once the autoclave was cooled down to room temperature, the gas inside was vented in a fume hood, and the solid/liquid products were rinsed from the autoclave by washing with reagent-grade acetone. The resulted suspension was filtered through a pre-weighed filter paper under vacuum (approximately 0.03 MPa) to separate the solid and liquid products. The remaining solids on the filter paper were named as char (ethanol and acetone insoluble fraction). This fraction was dried in an oven at 378 K overnight and then quantified. The filtrate was evaporated under reduced pressure (about 0.09 MPa) at 323 K to remove the solvents (ethanol and acetone), followed by being evaporated under reduced pressure (about 0.09 MPa) at 363 K to remove the water formed during liquefaction process. The resulted liquid phase product was designated as bio-oil. Yields of liquefaction products (bio-oil and char) and conversion rate were all expressed in wt.% and calculated as follows:
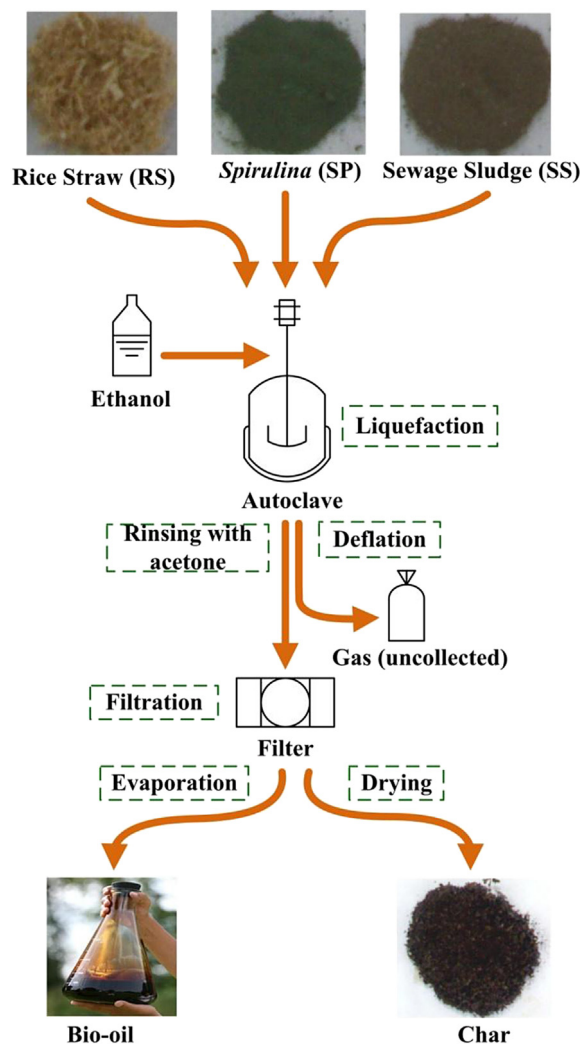
$$\text{Yield of bio} - \text{oil} = (\text{mass of bio} - \text{oil})/(\text{mass of feedstock}) \times 100\%$$

(1)

$$\text{Yield of char} = (\text{mass of char})/(\text{mass of feedstock}) \times 100\%$$

(2)

$$\text{Conversion rate} = 100 \text{ wt.\%} - \text{yield of char} \quad (3)$$

All liquefaction experiments were repeated three times under nominally identical conditions to ensure the repeatability of the results. The standard deviations were also calculated and reported as experimental uncertainties. The maximum standard deviations for bio-oil and char yields were both less than 5%.

2.4. Analysis of liquefaction products

The elemental compositions of bio-oils and chars were analyzed by a CHNOS elemental analyzer (Vario EL III, Germany). Elemental analysis was conducted two times to reduce analytical errors. The reported results are the mean values. The calorific value was calculated according to the Dulong formula [12,13]:

$$\text{Calorific value } (MJ/kg) = 0.3383C + 1.442(H - (O/8)) \qquad (4)$$

where C, H and O are the mass percentages of carbon, hydrogen, and oxygen, respectively.

The density of bio-oils was determined according to ASTM-DP 1298 [25]. The dynamic viscosity of bio-oils was detected by a viscometer (SNB-2, China). The surface morphology of chars was investigated by a scanning electron microscope (SEM, FEI-Quanta200, Holland). GC−MS analyses of bio-oil were conducted on a GCMS-QP2010 Plus spectrometer (Shimadzu, Japan) equipped with RTX-5MS capillary column (5% biphenyl 95% dimethyl polysiloxane, 30 m × 0.25 mm × 0.25 μm). He was adopted as the carrier gas. The flow rate of carrier gas He was 1.2 mL/min. The specific column temperature program of GC used in this study was as follows: 313 K (hold 3 min) → 463 K (12 K/min, hold 1 min) → 563 K (8 K/min, hold 20 min). The temperature of injection chamber was 543 K, and the temperature of transfer line was 553 K. In addition, the temperature of ion source was 503 K and the mass range was 40−450 m/z.

3. Results and discussion

3.1. Feedstock characterization

The physicochemical and compositional characteristics of the feedstock samples are given in Tables 1 and 2. The N concentration of the algal feedstock was higher in comparison to lignocellulosic biomass and sewage sludge, most likely due to higher protein content in algae. Hence, presence of nitrogenous compounds (formed due to thermal degradation of proteins) could be expected in the liquefaction products of algal biomass [26]. For all the samples, the content of oxygen ranged from 39.39% to 48.85%. The molar ratio of H/C and O/C was in the range of 1.35−2.37, 0.68−0.82 respectively with low high heating value (HHV (Higher heating value), 13.71−19.80 MJ/kg).

The composition analysis of each feedstock indicated that Spirulina had the highest overall organic matter content on a dry weight basis (91.4%) compared to rice straw (88.3%) and sewage sludge (60.3%) as shown in Table 1. According to Table 2, the organic matter in Spirulina was comprised primarily of crude protein (63.4%) with relatively smaller amounts of carbohydrates (20.5%) and crude lipid (7.5%). In contrast, the content of ash in sewage sludge was as high as 39.2%. And the organic components in sewage sludge were distributed in the order of crude protein (33.6%), carbohydrates (20.3%) and crude lipid (6.9%). Lastly, rice straw consisted primarily of hemicellulose (41.3%), cellulose (24.6%) and lignin (9.2%).

3.2. Product distribution

Fig. 3 presents the product distributions obtained from thermochemical liquefaction of different biomasses. It can be clearly seen that sewage sludge had the highest bio-oil yield (39.46 ± 1.16%). Spirulina had a moderately lower bio-oil yield (34.51 ± 1.31%) despite having much higher initial protein content (63.4%) than sewage sludge (33.6%). Rice straw provided a much lower bio-oil yield (21.14 ± 0.93%) due to the larger carbohydrate content with low conversion efficiency. Biller and Ross [27] have identified the following general trend for conversion efficiency: lipids > proteins > carbohydrates. Vardon et al. [12] surmised that low carbohydrate conversion efficiency was mainly related to higher hemicellulose and lignin content. These above results point to the ability of thermochemical liquefaction to convert high organic content feedstocks into bio-oil, regardless of lipid content,
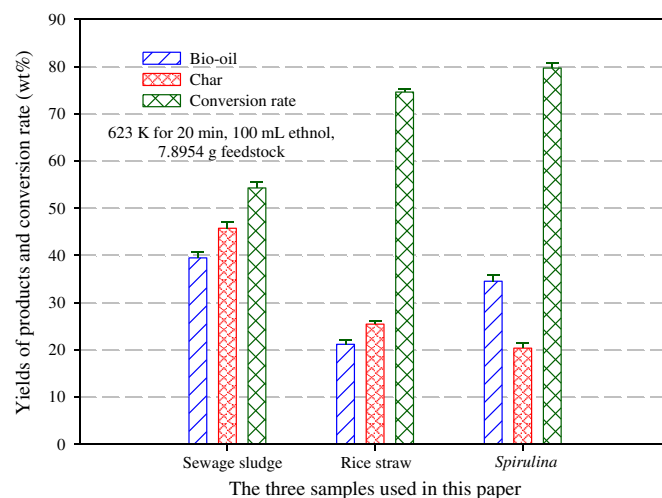

Fig. 3. The distributions of liquefaction products.

through the partial utilization of both protein and carbohydrate fractions [27].

The yields of chars were determined to 45.73 ± 1.37%, 25.41 ± 0.74% and 20.33 ± 1.02% of the feedstock for sewage sludge, rice straw and Spirulina, respectively. It was implied that higher amount of ash in feedstock may lead to more char formation. In the case of lignocellulosic biomass, hemicellulose and lignin are expected to be the biopolymers that contributed most to char formation. For the algal sample and sewage sludge, it appears likely that both protein and carbohydrates could have degraded into char [26].

3.3. Characterization of bio-oil and char

The density and dynamic viscosity of bio-oils produced from different feedstocks are listed in Table 3. At room temperature, bio-oils were dark brown liquids having a distinctive smoky odor. The densities of bio-oils ranged from 0.91 g/cm³ to 1.02 g/cm³ similar to that of fossil oil (0.75−1.0 g/cm³) [28]. The dynamic viscosities of bio-oils measured at 323 K were found to be 818.3−1223.9 mPa•s, which were significantly higher than that of heavy petroleum fuel oil (180 mPa•s) [29]. Higher viscosity data suggest that the bio-oils will need further modification for engine uses.

Table 3
Physicochemical prosperities of bio-oils and chars derived from different feedstocks.

Items	SS	RS	SP
Ultimate analysis of bio-oil (wt.%)			
C	72.51	73.06	70.31
H	9.44	8.38	8.72
N	6.96	2.46	9.7
O[a]	11.09	16.1	11.27
H/C[b]	1.56	1.38	1.49
O/C[b]	0.11	0.17	0.12
Caloric value (MJ/kg)	36.14	33.90	34.33
Density (g/cm³)[c]	0.91	1.02	0.97
Dynamic viscosity (mPa•s)[c]	818.3	1223.9	962.5
Ultimate analysis of char (wt.%)			
C	15.2	53.61	41.69
H	1.14	3.45	2.63
N	1.95	1.9	5.45
H/C	0.90	0.77	0.76
O and metal elements	81.71	41.04	50.23

[a] Determined by difference and assuming that the sulfur content is negligible.
[b] Dimensionless quantity.
[c] Determined at 323 K.

The elemental compositions of bio-oils and chars are also summarized in Table 3. Compared to the original biomass materials, all bio-oils had much higher contents of carbon and much lower concentrations of oxygen, leading to significantly increased caloric values (33.90–36.14 MJ/kg). The *Spirulina* bio-oil had the highest nitrogen content (9.7%) of the three bio-oils, which was due to the high content of protein in *Spirulina*. Rice straw, with its high lignin and cellulose content, produced a bio-oil with the greatest oxygen content (16.1%) and lowest HHV (33.90 MJ/kg). The bio-oil produced from sewage sludge possessed the highest hydrogen content (9.44%) and the lowest oxygen content (11.09%), which resulted in the highest caloric value (36.14 MJ/kg). However, compared with fossil oil, the oxygen and nitrogen content in bio-oils were still too high. The content of oxygen and nitrogen in fossil oil distribute in the range of 0.05–1.5% and 0.01–0.7%, respectively [28]. The high oxygen and nitrogen content is a primary factor that distinguishes bio-oils from petroleum crudes, and upgrading processes for lowering heteroatom content represent a significant challenge to the biofuel industry [12].

The hydrogen content of chars for the three samples was 1.14–3.45%. Carbon existed in chars mainly in the form of coke with the content of 15.2–53.61%. The H/C molar ratio of the chars was 0.76–0.90, suggesting that there was still some possibility to further increase the conversion to a higher degree by selecting appropriate experimental conditions. In addition, the oxygen existed mainly in the ash components, combined with metal elements in the formed of metal oxides which were inactive during the whole process [24]. Morphological analysis of char was carried out by applying SEM. SEM images of feedstock and char are shown in Fig. 4. As can be seen in this figure, the large structural differences have been occurred during liquefaction. The chars had been twisted out of shape. The SEM images also illustrated porous structure of chars.

3.4. GC/MS analysis of bio-oil

In contrast to the bulk elemental analysis, the chemical characterization of bio-oils from different feedstocks could exhibit a more marked degree of variation. Bio-oils produced from the
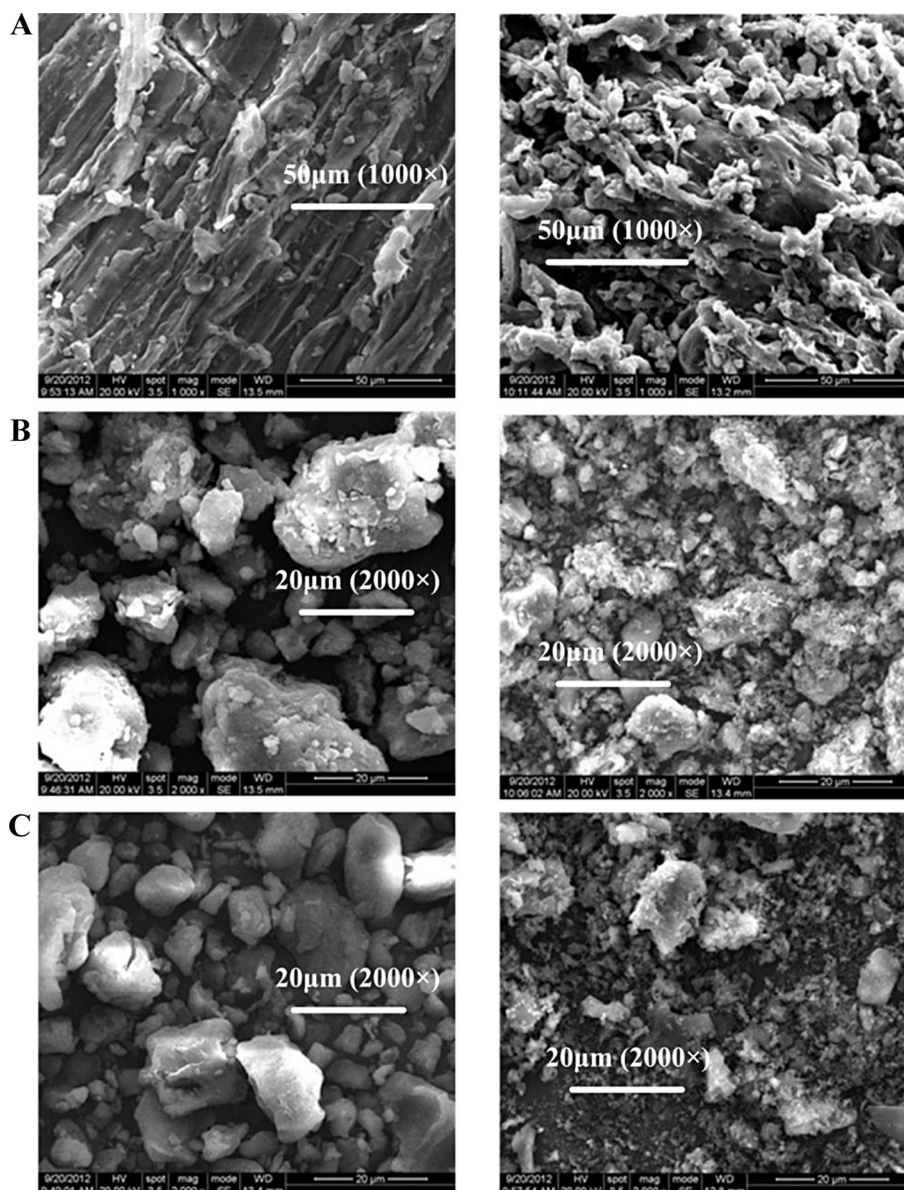

Fig. 4. SEM images of feedstocks (left) and chars (right) (A: Rice straw, B: Sewage sludge, C: *Spirulina*).

liquefaction of different feedstocks (rice straw, *Spirulina* and sewage sludge) were analyzed using GC–MS. Hundreds of peaks were detected in the total ion chromatograms of bio-oils (Fig. 5), implying that the bio-oils were quite complex mixtures of organic compounds. The identification of the main compounds was performed using a NIST mass spectral database. Tables 4–6 list the typical compounds in the three bio-oils. Only those compounds with peak area (%) higher than 1% (marked in Fig. 5) were presented in these tables. The percentage values (by integration from total ion chromatogram) indicate the proportions of individual compounds in the bio-oil but do not present the actual concentration.

Comparative analysis of Tables 4–6 showed that the use of different types of biomass had an important effect on the intensity of various components in the bio-oils. These compounds detected
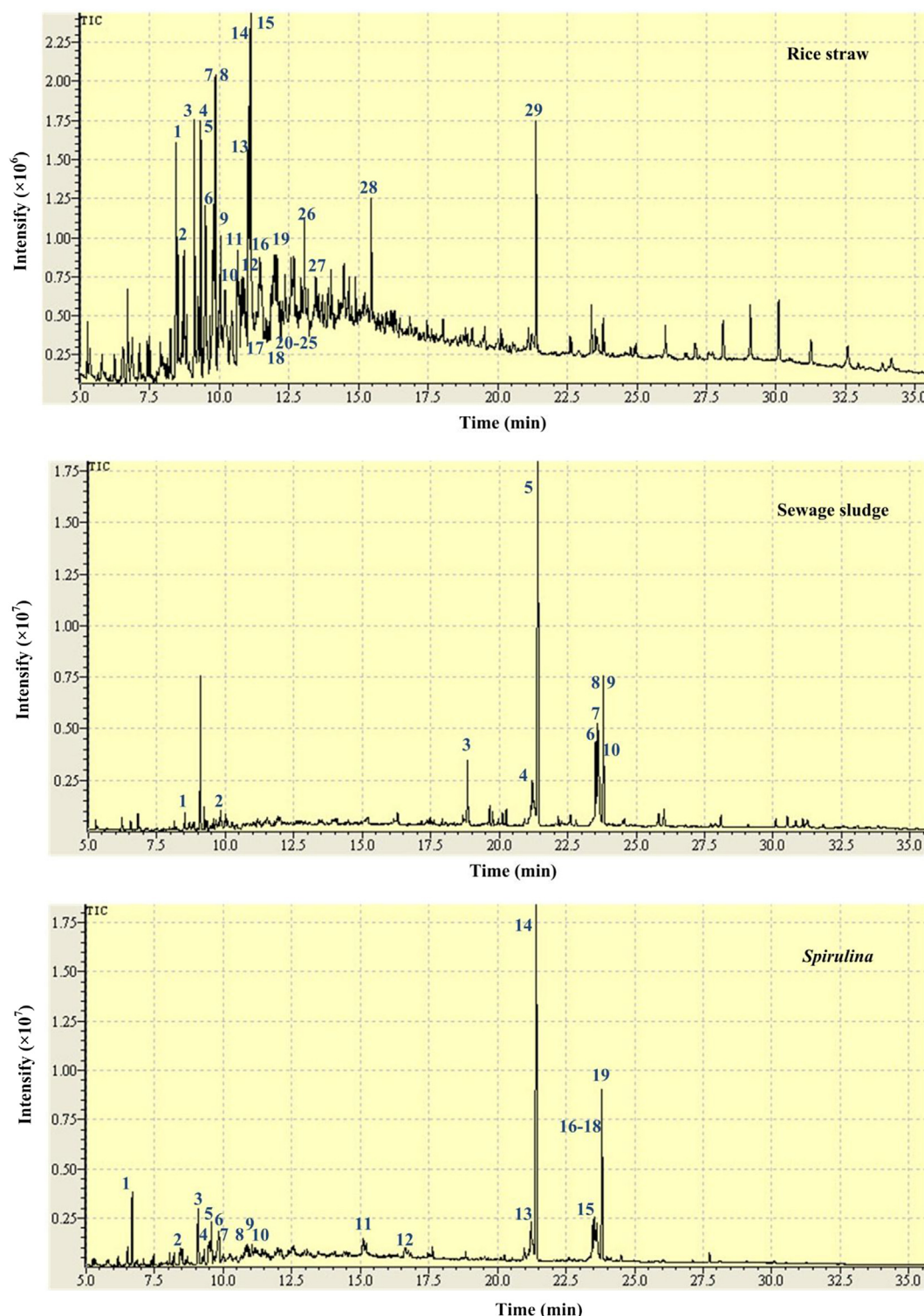

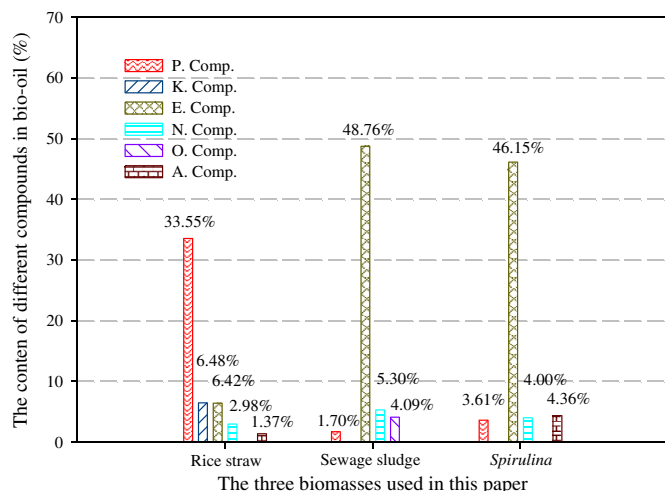**Fig. 5.** Total ion chromatograms of bio-oils.

Fig. 6. The relative content of different compositions in the bio-oils. (P. compound: phenolic compounds; K. compound: ketones; E. compound: esters; N. compound: nitrogenous compounds; O. compound: organic acids; A. compound: alcohols).

in bio-oils could be roughly divided into ten types: phenolic compounds, furan derivations, acids, alkanes, alcohols, esters, nitrogenous compounds, ketones, benzene series compounds and glucide ramification. The relative content of six major compounds in the three bio-oils are depicted in Fig. 6. Rice straw bio-oil contained the highest phenolic compounds (33.55%), while esters were the major compounds identified in the bio-oils derived from both sewage sludge (48.76%) and *Spirulina* (46.15%).

As can be seen from Fig. 6, the sewage sludge and *Spirulina* bio-oils had a much lower content of phenolic compounds compared to the rice straw bio-oil. This fact may be ascribed to the lower content of lignin in sewage sludge and *Spirulina*, now that the phenolic compounds were primarily originated from the degradation of lignin component (by cleavage of the aryl ether linkages in lignin) [20]. The basic unit of lignin is the phenyl propane (substituted), which is a rich source of phenolic compounds in the liquid hydrocarbons. In addition, the phenolic compounds can also be derived from the carbohydrate and protein fraction [12].

In comparison with sewage sludge or *Spirulina* deprived bio-oil, the bio-oil obtained from the liquefaction of rice straw additionally contained a low content of ketones (6.48%), furan derivations (3.75%) and benzene series compounds (2.1%). According to Table 4, several ketones were observed such as 2, 3-dimethyl-2-cyclopenten-1-one, 4-ethyl-3, 4-dimethyl-2-cyclohexen-1-one, and 1-(2-hydroxy-6-methoxyphenyl)-ethanone. There was not enough evidence to prove that the formation of ketones was uniquely attributed to the decomposition of cellulose. The small functional groups cracked from the lignin monomers could also be the source of ketones. The content of benzene and benzene derivatives were very low, far lower than that of the phenolic compounds, which indicated that the −OH on the benzene ring was difficult to be removed at the low temperature (623 K in this study). Furan derivatives originated undoubtedly from the decomposition of cellulose, further decomposition of these compounds might contribute to the formation of esters such as ethyl 2-hexenoate (2.83%), pentanedioic acid, diethyl ester (1.03%) and hexadecanoic acid, ethyl ester (2.56%) [24].

As shown in Table 5, the major compound identified in sewage sludge bio-oil was pentadecanoic acid, ethyl ester (22.04%), followed by octadecanoic acid, ethyl ester (7.51%), (E)-9-octadecenoic acid, ethyl ester (6.27%) and 5-ethyl-2-methyl-pyridine (5.30%). As regards *Spirulina* bio-oil, the most prevalent compound was still the pentadecanoic acid, ethyl ester (21.20%); and the contents of octadecanoic acid, ethyl ester (8.53%), butanoic acid, 3-methylphenyl ester (3.48%) and hexadecanoic acid, ethyl ester (2.03%) were the next (Table 6). Bio-oils containing plentiful organic acid can be produced in liquefaction of microalgae with H_2O as solvent [21]. However, lots of organic acid ethyl ester compounds, which are similar to biodiesel, were obtained with ethanol as liquefaction solvent. Possible explanations may be the promoted esterification reactions between organic acid and solvent ethanol [10,30].

Table 4
Major chemical compositions of bio-oils derived from rice straw.

No.	RT (min)	Name of compound	Peak area (%)
1	8.44	Phenol (C_6H_6O)	3.00
2	8.73	2-Cyclopenten-1-one, 2,3-dimethyl-($C_7H_{10}O$)	1.36
3	9.09	Pyridine, 5-ethyl-2-methyl-($C_8H_{11}N$)	2.98
4	9.24	Benzyl Alcohol (C_7H_8O)	1.37
5	9.33	Ethyl 2-hexenoate ($C_8H_{14}O_2$)	2.83
6	9.50	Phenol, 2-methyl-(C_7H_8O)	2.77
7	9.78	Phenol, 3-methyl-(C_7H_8O)	3.59
8	9.85	Furan, 2-butyltetrahydro-($C_8H_{16}O$)	3.75
9	10.04	Phenol, 2-methoxy-($C_7H_8O_2$)	1.63
10	10.22	Cyclohexane, (1-methylethylidene)-(C_9H_{16})	1.19
11	10.65	Phenol, 2,3-dimethyl-($C_8H_{10}O$)	2.17
12	10.81	Phenol, 2,6-dimethyl-($C_8H_{10}O$)	1.91
13	10.89	2(1H)-Naphthalenone, 4a,5,6,7,8, 8a-hexahydro-8a-methyl-, trans-($C_{11}H_{16}O$)	1.53
14	11.04	Phenol, 4-ethyl-($C_8H_{10}O$)	4.00
15	11.12	Phenol, 3-ethyl-($C_8H_{10}O$)	4.60
16	11.33	Phenol, 2-ethyl-5-methyl-($C_9H_{12}O$)	1.21
17	11.45	2-Cyclohexen-1-one, 4-ethyl-3,4-dimethyl-($C_{10}H_{16}O$)	1.01
18	11.96	Phenol, 2,3,6-trimethyl-($C_9H_{12}O$)	1.73
19	12.00	Benzene, 1-ethyl-4-methoxy-($C_9H_{12}O$)	1.08
20	12.07	2,3a-Dimethylhexahydrobenzofuran-7a-ol ($C_{10}H_{18}O_2$)	1.18
21	12.36	Phenol, 2,4,6-trimethyl-($C_9H_{12}O$)	1.21
22	12.49	Pentanedioic acid, diethyl ester ($C_9H_{16}O_4$)	1.03
23	12.58	Phenol, 4-ethyl-2-methoxy-($C_9H_{12}O$)	1.55
24	12.68	Benzene, 1,4-dimethoxy-2-methyl-($C_9H_{12}O$)	1.02
25	12.93	Thymol ($C_{10}H_{14}O$)	1.14
26	13.05	Phenol, 2-methyl-5-(1-methylethyl)-($C_{10}H_{14}O$)	2.04
27	13.18	2,5-Diethylphenol ($C_{10}H_{14}O$)	1.00
28	15.45	Ethanone, 1-(2-hydroxy-6-methoxyphenyl)-($C_9H_{10}O_3$)	1.40
29	21.38	Hexadecanoic acid, ethyl ester ($C_{18}H_{36}O_2$)	2.56
30	Total		57.84

Table 5
Major chemical compositions of bio-oils derived from sewage sludge.

No.	RT (min)	Name of compound	Peak area (%)
1	9.08	Pyridine, 5-ethyl-2-methyl-($C_8H_{11}N$)	5.30
2	9.83	Phenol, 3-methyl-(C_7H_8O)	1.70
3	18.84	Tetradecanoic acid, ethyl ester ($C_{16}H_{32}O_2$)	2.86
4	21.21	Hexadecanoic acid, ethyl ester ($C_{18}H_{36}O_2$)	3.23
5	21.26	Ethyl 9-hexadecenoate ($C_{18}H_{34}O_2$)	1.99
6	21.41	Pentadecanoic acid, ethyl ester ($C_{17}H_{34}O_2$)	22.04
7	23.52	Ethyl Oleate ($C_{20}H_{38}O_2$)	4.86
8	23.60	(E)-9-Octadecenoic acid, ethyl ester ($C_{20}H_{38}O_2$)	6.27
9	23.63	cis-13-Octadecenoic acid ($C_{18}H_{34}O_2$)	4.09
10	23.80	Octadecanoic acid, ethyl ester ($C_{20}H_{40}O_2$)	7.51
11	Total		59.85

Strikingly, certain amounts of nitrogenous compounds were detected in all three bio-oils, 2.98% for rice straw, 5.30% for sewage sludge, and 4.00% for *Spirulina*. Nitrogenous compounds may result from the decomposition of proteins. Specifically speaking, they may be derived from the decarboxylation and rearrangement of amino acids [31]. Catalytic upgrading can be used to remove nitrogen through hydrodenitrogenation (HDN) and limit regulated NO_x emissions during biofuel combustion. However, due to their basicity, nitrogen compounds are highly problematic for conventional hydro-treatment catalysts since they strongly adsorb to active acidic sites and require more severe treatment conditions [12].

3.5. Volatility distribution of the bio-oils

The GC–MS analysis data were used to present the boiling point distribution of biomass-derived bio-oils in the form of C-NPgram (Carbon-Normal Paraffin gram). Fig. 7 shows the C-NPgram of bio-oils obtained from various types of biomass. The C-NPgram was proposed by Murata et al. [32] to characterize the liquid products obtained from thermal degradation of polymers. And it was constructed by plotting the weight fraction of hydrocarbons, which are located within the range of retention values of two successive normal paraffins, C_{n-1} and C_n, against the carbon number, n. The carbon numbers in the abscissa represent the equivalent boiling point range of normal paraffin hydrocarbons. More details about C-NPgram can be found in two literature [32,33].

The hydrocarbons were distributed in the boiling point region n-C_4 to n-C_{21} for all the bio-oils. It can be clearly seen that the volatility distribution of rice straw showed a distinguished trend. The majority of hydrocarbons were about 22.24% at C_8 in rice straw-derived bio-oil. However, the majority of hydrocarbons for sewage sludge and *Spirulina* were distributed at C_{17} and C_{20}. The hydrocarbons at C_{17} were about 22.04% and 21.20% for sewage sludge and *Spirulina*, respectively. The peak at C_{17} was mainly due to pentadecanoic acid, ethyl ester. Sewage sludge produced the hydrocarbons about 18.64% at C_{20} whereas it was 16.25% in case of *Spirulina*. Although the majority of hydrocarbons were at the same carbon number (C_{17} and C_{20}) for both sewage sludge and *Spirulina*, the volatility distributions of other hydrocarbons were different. The hydrocarbons in the range of C_5 to C_9 were around 17.73% for *Spirulina* while they are about 7.0% for sewage sludge. At C_{18} the
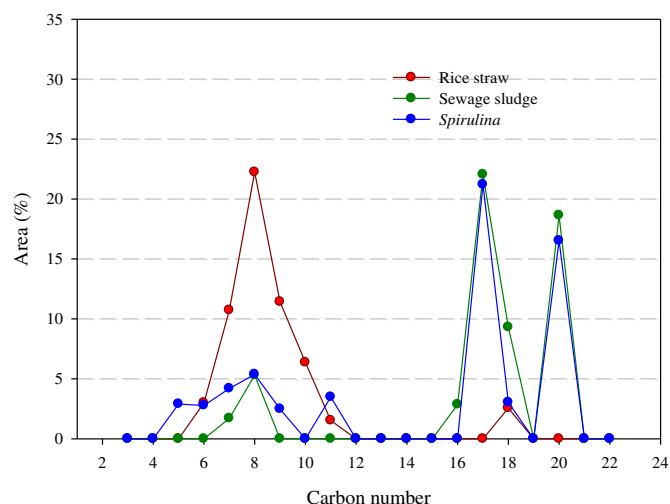

Fig. 7. C-NPgram of bio-oils obtained from liquefaction of different feedstocks.

area of hydrocarbons for sewage sludge was about 9.31%, whereas it was around 3.04% for *Spirulina*.

4. Conclusions

Three different biomasses (rice straw, sewage sludge and *Spirulina*) were liquefied at identical conditions. And their thermochemical liquefaction characteristics were systematically compared. The conclusions are as follows:

(1) The conversion rates of the three biomasses were as follows: *Spirulina* (79.7 ± 1.02%) > rice straw (74.6 ± 0.74%) > sewage sludge (54.3 ± 1.37%). However, sewage sludge produced the highest bio-oil yield (39.5 ± 1.16%). And the caloric value of bio-oil from sewage sludge reached up to 36.14 MJ/kg, higher than the other two bio-oils from rice straw (33.90 MJ/kg) and *Spirulina* (34.33 MJ/kg), respectively.
(2) The composition of the bio-oil from rice straw consisted mainly of phenolic compound, while the major hydrocarbons were esters in case of sewage sludge and *Spirulina*.
(3) The volatility distribution of major hydrocarbons for sewage sludge and *Spirulina* were similar (mainly at C_{17} and C_{20}), whereas a distinct trend was observed in rice straw-derived bio-oil (mainly at C_8).

In a word, the types and components of biomass have an important effect on the distributions of products, the bio-oil compositions and the volatility distribution of hydrocarbons. Techno-economic analysis of the bio-oil production via liquefaction of different biomasses should be further comparatively studied.

Acknowledgments

Table 6
Major chemical compositions of bio-oils derived from *Spirulina*.

No.	RT (min)	Name of compound	Peak area (%)
1	6.68	2-Furanmethanol ($C_5H_6O_2$)	2.90
2	8.43	Phenol (C_6H_6O)	1.17
3	9.08	Pyridine, 5-ethyl-2-methyl-($C_8H_{11}N$)	2.98
4	9.47	4-O-Methylmannose ($C_7H_{14}O_6$)	1.08
5	9.51	Phenol, 2-methyl-(C_7H_8O)	1.20
6	9.58	Pentanoic acid, 4-oxo-, ethyl ester ($C_7H_{12}O_3$)	1.91
7	9.84	Butanoic acid, 3-methylphenyl ester ($C_{11}H_{14}O_2$)	3.48
8	10.82	4-Isopropylidene-cyclohexanol ($C_9H_{16}O$)	1.46
9	10.88	Phenol, 2,5-dimethyl-($C_8H_{10}O$)	1.24
10	11.42	1H-1,2,3,4-Tetrazole-1,5-diamine, N(1)-[(2-methoxyphenyl)methyl]-($C_9H_{12}N_6O$)	1.02
11	15.11	.beta.-ᴅ-Glucopyranose, 1,6-anhydro-($C_6H_{10}O_5$)	1.61
12	16.63	Ethyl .alpha.-ᴅ-glucopyranoside ($C_8H_{16}O_6$)	1.16
13	21.23	Hexadecanoic acid, ethyl ester ($C_{18}H_{36}O_2$)	3.04
14	21.42	Pentadecanoic acid, ethyl ester ($C_{17}H_{34}O_2$)	21.20
15	23.46	Linoleic acid ethyl ester ($C_{20}H_{36}O_2$)	1.63
16	23.52	Ethyl Oleate ($C_{20}H_{38}O_2$)	2.77
17	23.59	9-Octadecenoic acid, ethyl ester ($C_{20}H_{38}O_2$)	1.32
18	23.62	9,12-Octadecadienoic acid, ethyl ester ($C_{20}H_{36}O_2$)	2.27
19	23.81	Octadecanoic acid, ethyl ester ($C_{20}H_{40}O_2$)	8.53
20		Total	61.97

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