Alteration of sewage sludge biomass into oil-like products by hydrous pyrolysis methods

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HIGHLIGHTS
▶ We used hydrous pyrolysis to study alteration products of sewage sludge (SS) OM.
▶ Two sets of experiments were conducted at \( T = 200-350 \) °C for 48 h.
▶ The first set included only SS and water and the second with oxalic acid (OA).
▶ The yields and alteration products increased with temperature and presence of OA.
▶ The results show that the yields are higher under reductive hydrous pyrolysis.

Article info
Article history:
Received 5 May 2012
Received in revised form 23 July 2012
Accepted 25 July 2012
Available online 13 August 2012

Keywords:
Hydrous pyrolysis
Sewage sludge
Hydrocarbons
UCM
Steranes

Abstract
Various pyrolysis (also termed thermolysis) methods are common techniques that have been used to convert sewage sludge organic matter (OM) into useful fuels for energy. Reductive hydrous pyrolysis of OM increases the conversion yields of the sewage sludge. Our purpose is to study the effects of low temperature (<350 °C) and experimental conditions in confined hydrous pyrolysis on the chemical compound compositions of the alteration products from municipal sewage sludge. These compositions have been determined by gas chromatography-mass spectrometry. Two sets of experiments were conducted at temperatures ranging from 200 to 350 °C with contact periods of 48 h. The reaction mixtures of the first set included only sewage sludge and water, whereas the second set also contained oxalic acid to provide excess hydrogen to enhance reduction of the organic matter of sewage sludge. The yields and the number of observed alteration products increased with higher temperature and presence of aqueous oxalic acid in the reaction mixtures. At lower temperatures \( n \)-alkanoic acids, \( n \)-alkanols and sterols were the major compounds. Hydrocarbon concentrations increased at higher temperatures in both experiment sets, except for UCM (unresolved complex mixture), which decreased >300 °C. The \( n \)-alkanes increased dramatically with temperature increase both in the presence and absence of oxalic acid, where their yields were high in the former medium. Sterane concentrations also increased at elevated temperatures, being highest in the presence of oxalic acid. The products confirm that alteration of sewage sludge biomass in aqueous medium occurs rapidly and efficiently under reductive pyrolysis conditions, and in the temperature window of 250–350 °C. These results show that the product yields are higher by a factor of 1.4 under reductive hydrous pyrolysis versus hydrous pyrolysis conditions.

1. Introduction
Efficient disposal of municipal waste water or sewage is important to the health of any community. Typical municipal sewage contains oxidizable materials, nutrients, sediment, grease, oil, scum, pathogenic bacteria, viruses, algal and fungal detritus, salts, pesticides, refractory organic compounds, heavy metals, and an astonishing variety of flotsam [1,2].

Primary treatment of waste water and sewage consists of the removal of insoluble matter such as grit, grease, and scum from the waters by screening. This is followed by coagulation, sedimentation and skimming of floating solids, which are combined with the downstream sludge [2]. The sedimented particles are the
sludge which is aerated in the activated sludge process to reduce the organic matter content by microbiological aerobic digestion. The dewatered sludge residue may be incinerated, used as fertilizer or dumped in landfills [2–4].

Sewage sludge disposal is one of the complex environmental problems. Currently, most of the sewage sludge wastes are disposed in different landfill sites [5]. Because of potential health problems, the disposal of dried sewage sludge in landfills is not a realistic solution [4]. Coastal zones and the oceans are other locations for disposal of sewage sludge [5,6]. This practice should be avoided because it disturbs the marine ecosystem [7–10].

Sewage sludge consists of organic wastes with abundant organic matter (OM) contents, which can be converted into useful products for energy sources [11,12]. The recent applications of new methods and techniques to utilize sewage sludge biomass as energy sources have drawn the attention of scientists and researchers. Various pyrolysis methods are common techniques that have been used to convert biomass into useful fuels for energy [11–16].

Generally, conversion processes may be classified into: (1) pyrolysis, where organic matter (OM) is heated in an oxygen-free environment; (2) direct liquefaction, in which hydrogen gas is used to react with OM at high temperature and pressure in the presence of a catalyst; and (3) indirect liquefaction (gasification), where the OM is completely gasified to produce a synthesis gas consisting primarily of a mixture of hydrogen and carbon monoxide [17]. Pyrolysis of OM produces solid carbonaceous materials (char), liquid product (oil and tar), volatiles and gases [18]. Liquid products from pyrolysis contain significant amounts of oxygen-, sulfur-, and nitrogen-containing compounds. Other data show that reductive hydrous pyrolysis of OM increases the conversion yields [19].

The main goal of this research is to study the effects of temperature and different experimental conditions in hydrous and reductive hydrous confinement pyrolysis on the chemical compound composition of the alteration products from sewage particulate matter. Therefore, sewage solids are subjected to hydrous pyrolysis at different experimental conditions (i.e., in the absence and presence of oxalic acid). The data and information obtained from this experimental approach are discussed to define yields, compound compositions, compound transformations and alteration processes of sewage solids by hydrous pyrolysis.

2. Experimental procedures

2.1. Sewage sludge samples

The sewage sludge samples were collected from the Riyadh Sewage Treatment Plants (RSTPs) in the city of Riyadh, Saudi Arabia and from the Sewage Treatment Plant in Idaho Falls, Idaho, USA. These two sewage sludge samples were selected because they vary in organic matter contents as will be shown in the results section. The sewage sludge samples were air dried, powdered and kept in the freezer until used for experiments. A sub-sample of the sewage sludge from RSTP was analyzed using a CHNS analyzer in the College of Sciences, King Saud University.

2.2. Sample extraction

About 2 g of each sewage sludge sample was extracted three times using ultrasonic agitation for a 15-min period each with 15 mL of dichloromethane and 5 mL of methanol. The extraction was carried out in a 50-mL precleaned beaker. The extract was then filtered using a filtration unit containing an annealed glass fiber filter for the removal of suspended particles. The filtrate was first concentrated on a rotary evaporator and then reduced using a stream of dry nitrogen gas to a volume of approximately 100 μL. The volume was then adjusted to 200 μL exactly by addition of dichloromethane/methanol (3:1, v/v). A 50-μL aliquot of each total extract of sewage sludge was derivatized with silylating reagent [N,O-bis(trimethylsilyl)trifluoroacetamide, Pierce Chemical Co.] before analysis by GC–MS. This derivatizing agent replaces the H in hydroxyl groups with a trimethylsilyl [(CH3)3Si, i.e., TMS] group for better GC resolution of polar compounds [20].

2.3. Pyrolysis experiments

We used 316 stainless steel vessels (Fig. 1) constructed with Sno-Trik high-pressure couplings [19,21,22], to study the alteration products of sewage sludge under hydrothermal conditions. The vessels were capable of handling system pressure to 60,000 psi (413,682 kPa, Sno-Trik Company). The internal capacities of the vessels were 380 ± 20 μL. Before each experiment, the reaction vessels, sewage sludge and solid oxalic acid were placed in a glove bag and flushed with N2 for about 5 min. Two experimental sets were prepared for particular reaction conditions. Experiment set 1 was a mixture of doubly distilled water and sewage sludge. The addition of pre-extracted (to remove organic contaminants) solid oxalic acid dehydrate (99.5%, EM Science) to experiment set 1 gave experiment set 2.

Aqueous oxalic acid (C3H2O4) degrades to formic acid (CH2O2) and CO2 at 160–230 °C following first order kinetics [23]:

\[
\text{C}_3\text{H}_2\text{O}_4 \rightarrow \text{CH}_2\text{O}_2 + \text{CO}_2 
\]

In the presence of excess water and at higher temperatures, formic acid decomposes to H2, CO2, CO and H2O according to the following reactions [24]:

\[
\text{CH}_2\text{O}_2 \rightarrow \text{H}_2 + \text{CO}_2 
\]

\[
\text{CH}_2\text{O}_2 \rightarrow \text{CO} + \text{H}_2\text{O} 
\]

The net decomposition of oxalic acid (via formic acid) proceeds according to the following reaction:

\[
2\text{CH}_2\text{O}_2 \rightarrow 3\text{CO}_2 + \text{CO} + \text{H}_2 + \text{H}_2\text{O} 
\]

This decomposition provides hydrogen for reduction and the estimated pH of the aqueous oxalic acid at 25 °C is about 0.54 (acidic condition). Blank experiments (i.e., without sewage sludge) were carried out with all reactants to insure that the alteration products were not impurities originating from oxalic acid, doubly distilled water or vessels. A weight of 0.50 ± 0.05 g of dried sewage sludge was added to the reaction vessel, plus for reductive hydrous pyrolysis experiments 0.04 g of oxalic acid, followed by slow flushing with N2, and filling the vessel with doubly distilled water. All vessels were filled to capacity, sealed and placed immediately into an oven for 48 h. The temperature settings were 200, 250, 300 and 350 °C for the two experiment sets. Upon removal from the oven, the vessels were cooled to room temperature. They were opened gradually and carefully in order to release the pressure (due to
CO₂ and other gases generated during the experiment). Despite this precaution, a minor portion of fluid sample was sometimes expelled during opening in experiments with oxalic acid mixtures. This has no major effect as shown by the increase of product concentrations without reducing the total extract volume.

Each sample was immediately transferred by Pasteur pipette to a glass vial containing MgSO₄ (to remove any water in the extracts). Each vessel was rinsed three times with dichloromethane/methanol (3:1, v/v) which was added to the vial giving a total volume of approximately 2 ml. Each sample was then concentrated under nitrogen flush and room temperature to approximately 50–100 μl before GC–MS analysis.

2.4. Instrumental analysis

The analysis of the alteration products and external standards was carried out by GC–MS on a Hewlett–Packard 6890 GC coupled to a 5973 Mass Selective Detector using a DB-5 (J and W Scientific, Agilent) fused silica capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) and helium as carrier gas. The GC was temperature programmed from 65 °C (2 min initial time) to 300 °C at 6 °C min⁻¹ (isothermal for 20 min final time). The MS was operated in the electron impact mode at 70 eV ion source energy. Data were acquired and processed with a Hewlett–Packard Chemstation and compounds were identified by GC retention index and by comparison of mass spectra with those of authentic standards, literature and library data, and characterized mixtures. Unknown compounds were characterized by interpretation of the fragmentation pattern of their mass spectra. Relative concentrations of the compounds for the Idaho sample were estimated from ratios of peak areas, which assume that the detection response is linear over the range of concentrations observed and that the response factors are similar for the different compounds. The concentrations of the compounds of the Riyadh sample were determined from peak area responses compared to those of external standards analyzed concurrently on the same instrument.

3. Results

3.1. Total carbon, nitrogen, hydrogen and sulfur of sewage sludge

The total elemental carbon, hydrogen, nitrogen, and sulfur (CHNS) analysis of the sewage sludge from RSTP showed that it contained 29.81 wt.% carbon, 4.23 wt.% hydrogen, 3.64 wt.% nitrogen, 4.37 wt.% sulfur and 57.95 wt.% oxygen (by difference). The atomic ratios are: H/C = 1.70, N/C = 0.105, S/C = 0.55 and O/C = 1.46. The major inorganic elements are aluminum (8970 ± 34 μg g⁻¹), iron (8514 ± 22 μg g⁻¹), zinc (1557 ± 20 μg g⁻¹), Cr (364 ± 27 μg g⁻¹), manganese (168 ± 13 μg g⁻¹) and copper (112 ± 18 μg g⁻¹) [25].

3.2. Extracts of sewage sludge

The extract yields of the two sewage sludge samples (i.e., RSTD and Idaho Falls) are found in Table 1. Salient features of the GC–MS data for the silylated total extracts are shown in Figs. 2a and 3a and the major compounds identified are listed in Table 1. The extracts are comprised of lipids from mainly human waste for the Riyadh sample and additional wash-in of other urban detritus from traffic for the Idaho sample. The major components of these lipids are n-alkanoic acids, n-alkanes, steroids, n-alkanes, polycyclic aromatic hydrocarbons (PAHs) and UCM (unresolved complex mixture) of branched and cyclic compounds.

For the Idaho sample, the UCM is dominant with steroids as the major resolved compounds (Fig. 2a). The steroids are composed of C₂₇–C₂₉ stanols, coprostanols, epi-coprostanols, sterols, sterones and stanones typical of digestive alteration [26]. The n-alkanoic acids range from C₁₂ to C₁₈, with a maximum (C₉₋₁₀ max) concentration of C₁₈ (palmitic acid) and significant amounts of unsaturated acids. A significant vegetation component is evident in the urban diet based on the presence of triterpenoids (amyrins, ursolic acid) and the enhancement of the phytosterol versus cholesterol derivatives (C₂₉/C₂₇ = 0.50). Also, the urban sewage contains major amounts of detergent residues (e.g. nonyl phenols), plasticizers (e.g. diethylhexyl phthalate, silicones), and vitamin supplements (e.g. α-tocopherol). These inputs are less significant for the Riyadh sample (Fig. 3a). Lastly, a major input from wash-in by rain of street detritus is evident for the urban sample, based on the presence of the dominant UCM from lubricating oils and the PAHs typical of combustion processes (e.g. wood smoke, Fig. SM1) [27,28].

3.3. Extracts of pyrolyzed sewage sludge

The sewage sludge samples from Riyadh were pyrolyzed with and without oxalic acid (reductive conditions) at 200, 250, 300, and 350 °C. The urban sample from Idaho was pyrolyzed only at 350 °C to compare optimal yield and product composition. The salient features of the GC–MS data for the pyrolysate extracts are shown in Figs. 2b, SM1–SM6 and 3b–h, and the major compound groups identified are listed in Table 1. The pyrolysis products are comprised primarily of n-alkanoic acids, methyl n-alkanoates, n-alkanols, steroids, UCM, n-alkan-2-ones, n-alkamides and n-alkanes, with lesser n-alkanes at the lower temperatures. The example TIC trace of the total extract from pyrolysis at 350 °C (with oxalic acid) shows a major UCM with resolved peaks of n-alkanoic acids, n-alkamides, n-alkanes and minor n-alkan-2-ones and steranes, with Diels’ hydrocarbon dominant (Fig. 2b, SM1–SM6). The results in Table 1 show that the total concentrations of extracted lipid compounds increased with the increase of heating temperatures and the availability of oxalic acid. In the absence of oxalic acid, the lipid concentrations increased from 22.1 ± 1.7 mg g⁻¹ in the starting sewage sludge sample to a maximum of 39.6 mg g⁻¹ at 350 °C and in the presence of oxalic acid (reducing conditions) they increased to a maximum of 49.6 mg g⁻¹ at 300 °C.

The n-alkanoic acids range from C₁₂ to C₁₈ at lower temperature, C₁₇–C₂₄ at 250 °C and C₂₀–C₂₄ at temperatures >300 °C, with C₉₋₁₀ max at mainly 16 in the absence of oxalic acid. Their total concentrations are 7.76 mg g⁻¹ in the starting sample and vary to a maximum of 11.71 mg g⁻¹ at 350 °C (Table 1, Fig. 4). With oxalic acid, they range from C₁₂ to C₂₄ at 250 °C and C₉₋₁₀ max also at 16. They decrease in concentration from 7.76 mg g⁻¹ in the initial sample to 4.39 mg g⁻¹ at 200 °C, 4.98 mg g⁻¹ at 250 °C and disappear at 300 °C. The C₁₅ and C₁₇ iso- and anteiso-alkanoic acids and derivate iso- and anteiso-alkamides (Figs. SM2 and SM4) are indicative biomarkers for bacteria, reflecting the extensive microbial degradation of the sludge OM. Methyl n-alkanoates range from C₄ to C₁₈ With C₉₋₁₀ max at 16 for unheated and pyrolyzed samples and both experimental media (Table 1, Fig. 4). Their concentrations increase from 0.18 mg g⁻¹ in the initial sewage sludge material to a maximum of 0.69 mg g⁻¹ at 200 °C and then decrease to traces at 350 °C. With oxalic acid they vary from C₁₂ to C₁₉ at concentrations of 3.84 mg g⁻¹ at 200 °C and decrease to 0.29 mg g⁻¹ at 300 °C (Table 1, Fig. 4).

The n-alkanols are present from C₁₂ to C₁₈ with C₉₋₁₀ max at 16 or 18:1 (Fig. 3a) in the unheated sewage sludge. They also range from C₁₂ to C₁₈ with C₉₋₁₀ max at 16 or 18 (Fig. 3b and c, Table 1) in the pyrolysates, with concentrations decreasing from 3.78 mg g⁻¹ at 200 °C to 0.22 mg g⁻¹ at 350 °C. In the presence of oxalic acid, they decrease from 4.34 mg g⁻¹ at 250 °C to none at 300 °C.

Steroids are present in the starting samples, ranging from C₂₇ to C₃₀ and include coprostanol, epi-coprostanol, stanols and the
corresponding carbonyls (Figs. 2a and 3a, Table 1). The concentrations of the steroids generally decrease with an increase in temperature both with and without oxalic acid. In the presence of oxalic acid, they disappear by reduction above 300 °C, with a concomitant increase in steranes [19]. Steranes are not found in the starting sewage sludge samples. They only occur in samples after pyrolysis and increase notably with rising experimental temperature. They range from C27 to C29 with Cmax at 27, and the concentrations of total steranes increase from 0.04 mg g \(^{-1}\) at 200 °C to a maximum of 2.36 mg g \(^{-1}\) at 350 °C and with oxalic acid they increase to 21.08 mg g \(^{-1}\) at 300 °C (Table 1, Fig. 4). Deils’ hydrocarbon (DHC), also known as 1,2-(3-methylcyclopenteno)phenanthrene, C18H16, forms by alteration of steroid precursors at high temperature via oxidation and cracking reactions [29]. DHC is observed here up to 0.4 mg g \(^{-1}\) in the higher temperature pyrolysates.

### Table 1

<table>
<thead>
<tr>
<th>Product</th>
<th>H2O</th>
<th>H2O + OA</th>
<th>H2O + OA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T</td>
<td>200</td>
<td>250</td>
</tr>
<tr>
<td>n-Alkanolic acids</td>
<td>T</td>
<td>6.1%</td>
<td>12%</td>
</tr>
<tr>
<td>Range</td>
<td>12–18</td>
<td>12–18</td>
<td>12–18</td>
</tr>
<tr>
<td>Cmax</td>
<td>16</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>% of Total</td>
<td>35%</td>
<td>39%</td>
<td>27%</td>
</tr>
<tr>
<td>Methyl n-alkanoates</td>
<td>n.d.</td>
<td>n.d.</td>
<td>T</td>
</tr>
<tr>
<td>Range</td>
<td>12–18</td>
<td>14–16</td>
<td>14–18</td>
</tr>
<tr>
<td>Cmax</td>
<td>16</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>% of Total</td>
<td>1%</td>
<td>2% &lt;1%</td>
<td>1%</td>
</tr>
<tr>
<td>n-Alkanols</td>
<td>n.d.</td>
<td>n.d.</td>
<td>2.76</td>
</tr>
<tr>
<td>Range</td>
<td>12–18</td>
<td>12–18</td>
<td>12–18</td>
</tr>
<tr>
<td>Cmax</td>
<td>18:1</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>% of Total</td>
<td>13%</td>
<td>14% 6%  &lt;1%</td>
<td>9%</td>
</tr>
<tr>
<td>n-Alkan-2-ones</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.27</td>
</tr>
<tr>
<td>Range</td>
<td>17–19</td>
<td>17–19</td>
<td>17–19</td>
</tr>
<tr>
<td>Cmax</td>
<td>17</td>
<td>17</td>
<td>17</td>
</tr>
<tr>
<td>% of Total</td>
<td>1.65</td>
<td>1.03</td>
<td>0.04</td>
</tr>
<tr>
<td>Steroids</td>
<td>33%</td>
<td>16–23</td>
<td>14–23</td>
</tr>
<tr>
<td>Range</td>
<td>27–29</td>
<td>27–29</td>
<td>27–29</td>
</tr>
<tr>
<td>Cmax</td>
<td>27</td>
<td>27</td>
<td>27</td>
</tr>
<tr>
<td>% of Total</td>
<td>1/4/16d</td>
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<tr>
<td>n-Alkanes</td>
<td>T</td>
<td>18%</td>
<td>19%</td>
</tr>
<tr>
<td>Range</td>
<td>16–32</td>
<td>17–32</td>
<td>17–32</td>
</tr>
<tr>
<td>Cmax</td>
<td>21</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>CPI(o/e)</td>
<td>1.04 ± 0.10</td>
<td>1.08</td>
<td>1.11</td>
</tr>
<tr>
<td>% of Total</td>
<td>3%</td>
<td>3%</td>
<td>3%</td>
</tr>
<tr>
<td>Steranes</td>
<td>n.d.</td>
<td>T</td>
<td>1%</td>
</tr>
<tr>
<td>Range</td>
<td>27–29</td>
<td>27–29</td>
<td>27–29</td>
</tr>
<tr>
<td>Cmax</td>
<td>27</td>
<td>27</td>
<td>27</td>
</tr>
<tr>
<td>% of Total</td>
<td>1%</td>
<td>3%</td>
<td>5%</td>
</tr>
<tr>
<td>DHC</td>
<td>n.d.</td>
<td>3%</td>
<td>3%</td>
</tr>
<tr>
<td>Range</td>
<td>18–20</td>
<td>18–20</td>
<td>18–20</td>
</tr>
<tr>
<td>Cmax</td>
<td>18</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>% of Total</td>
<td>0.4%</td>
<td>1.0%</td>
<td>T</td>
</tr>
<tr>
<td>UCM</td>
<td>64%</td>
<td>44%</td>
<td>46%</td>
</tr>
<tr>
<td>Yield (mg g (^{-1}))</td>
<td>2.61</td>
<td>2.75</td>
<td>10.47</td>
</tr>
</tbody>
</table>

DHC = Deils’ hydrocarbon.

N.D. = not determined.

**Relative Concentration (%)**

**Concentration is per weight of sewage sludge.**

**Relative to total extractable organic matter.**

**See Fig. 3 legend.**
to a maximum of 21.05 mg g\(^{-1}\) at 300 °C, with a decrease to 8.96 mg g\(^{-1}\) at 350 °C; however, with oxalic acid the UCM is less pronounced, maximizing at 12.17 mg g\(^{-1}\) at 250 °C and also decreasing to 6.37 mg g\(^{-1}\) at 300 °C (Fig. 4).

4. Discussion

4.1. Nature of the starting OM

The major components of the extract from the urban sample (Idaho) are UCM and steroids, with significant levels of pollutants such as nonyl phenols, PAHs and sulfur (Fig. 2a and b). The toxic pollutants, as well as other anthropogenic compounds (i.e., diethylhexyl phthalate, silicones) and UCM from petroleum lubricants, are adsorbed from waste water and rain wash-in onto the sludge particulate matter. The steroids, minor lipid compounds and triterpenoids are part of the sewage particulate matter and reflect the digestive alteration of the OM [30–32]. A significant diet of fruits and vegetables is evident for this urban area, based on the C\(_{29}/C_{27}\) coprostanol ratio of 0.50, and the presence of triterpenoids and 4,8,12,16-tetramethylheptadecan-4-olide. The latter compound is the major oxidation product from \(\alpha\)-tocopherol (vitamin E), another indicator for higher plant input [33,34].

The dominant compounds in the extract from the sewage sludge of metropolitan Riyadh are \(n\)-alkanoic acids, steroids and UCM, with significant \(n\)-alkanes, diethylhexyl phthalate and squa-lenes (Fig. 3a). The steroids are comprised primarily of C\(_{27}/C_{29}\) coprostanols and coprostanones, with minor stanols and thioster-anes, all characteristic of digestive tract alteration as mentioned above. The C\(_{29}/C_{27}\) coprostanol ratio is 0.37, less than the urban case above, which when coupled with the absences of triterpenoids and 4,8,12,16-tetramethylheptadecan-4-olide, supports a diet lower in fresh produce [35].

The \(n\)-alkanes in the initial samples range from C\(_{14}\) to C\(_{33}\), with odd carbon number predominances (CPI = carbon preference index) of 1.04 ± 0.10 and carbon number maximum (C\(_{\text{max}}\)) at 18 and 20, respectively (Table 1). This distribution indicates inputs from microbiota and petroleum lubricants to the sludge [36,37]. The relatively high initial concentrations of the C\(_{14}\)–C\(_{25}\) alkanes support the fact that biodegradation is a slow process. The CPI increased from 1.04 at ambient temperature to 1.49 at 350 °C under oxidative hydrous pyrolysis conditions and decreased to 0.63 at 300 °C under reductive conditions indicating two different reaction pathways.
4.2. Pyrolysis products

Pyrolysis is the process of thermal decomposition of complex organic matter to simple compounds and formation of new products under oxygen-free conditions and temperatures ranging from 200 to 900 °C, where high temperature is >700 °C and low <700 °C. Generally, products of OM pyrolysis are gas, oil, and carbonaceous residue as shown in following reaction:

\[ \text{n-Alkanoic acid} - \text{TMS} \]
\[ \text{n-Alkanoic acid} \]
\[ \text{n-Alkanol} - \text{TMS} \]
\[ \text{n-Alkanol} \]
\[ \text{Methyl n-alkanoate} \]
\[ \text{n-Alkyl amide} \]
\[ \text{Dimethyl alkyl amide} \]
\[ \text{n-Alkane} \]
\[ \text{n-Alkan-2-one} \]
Fig. 3 (continued)
Organic matter + energy = char + oil
+ non-condensible gas
+ carbonaceous residue

Oil products include high molecular weight organic compounds such as aliphatic compounds, olefins and polycyclic aromatic hydrocarbons.

The gas is useful as a fuel [37]. The carbonaceous char can be utilized as absorbent after upgrading to activated carbon [38–41]. The produced oil is used as fuel or as chemical feedstock for other purposes [42]. The effects of different parameters on pyrolysis products have been evaluated by various investigators [38–45]. Shen and Zhang [46] concluded that a maximum yield of 30% oil (wt.% of sludge feed) was achieved at a pyrolysis temperature of 525 °C. Wang et al. [47] found that a higher final pyrolysis temperature, an interval holding stage, and adding a catalyst promoted the pyrolysis conversion. The role of water in pyrolysis experiments has been shown necessary for maximum formation of oil-like products under hydrous conditions [48]. We assume that the presence of oxalic acid increases the formation of reduced organic liquid products at the expense of formation of oxidized organic products, such as char. Here we report the pyrolysis products from sewage sludge at relatively low temperatures (<350 °C).

The extractable compounds represent a minor amount of the total organic matter (e.g. Fig. 2a). During pyrolysis the neutral components (hydrocarbons) are diluted by additional hydrocarbons generated from the macromolecular OM (e.g. biopolymers of microbial membranes), and the polar compounds (steroids), both initial and newly liberated, are hydrogenated. Thus, the concentrations of the various neutral compound groups increase with rising temperature and longer reaction time to a maximum yield at 300–350 °C [19,49].

The minor n-alkane concentrations increase from 0.95 to 7.37 mg g⁻¹ of the total extractable organic matter with increasing temperature, especially under reducing conditions where the n-alkanols and n-alkanoic acids are hydrogenated. At high temperatures the n-alkane range increases to C₁₃–C₃₅ and C_max shifts from 20–21 to 17–18 (Fig. 2e) due to the onset of cracking reactions. The n-alkanoic acids and their derivatives (e.g. methyl esters, amides), as well as n-alkan-2-ones, persist over the pyrolysis temperature range (~3.15–11.71 mg g⁻¹) with a concentration decrease to maximal thermal stress (e.g. Figs. SM2, SM4, SM6 and Table 1).
The C27 steroids are major followed by the C28 and C29 phytosteroids (e.g. Figs. 2a and 3a). The 5β-stanols (e.g. coprostanol and epi-coprostanol) are major components of the total stanols in feces and derive from anaerobic bacterial alteration of cholesterol [49]. Sterane biomarkers are not found in the initial sewage sludge (Table 1), but become dominant upon pyrolysis (mainly as 5α-cholestan e and 5α-stigmastane) with minor amounts of the 5β-stananes [19]. Cracking and reformation reactions become evident >300 °C. This is reflected by the decrease in yield of the UCM, skewing of the n-alkane distribution to a lower carbon number maximum and loss of the steroid side chain with concomitant oxidation (aromatization) to Diels’ hydrocarbon (DHC, e.g. Fig. SM5).

More hydrocarbons, i.e., n-alkanes and stananes, were generated with increasing temperature and acidity of the reactants. The smallest amount of hydrocarbon products was in the temperature range from 200 to 250 °C and increased with temperature and addition of oxalic acid (acidity), especially at 300 °C. This considerable increase in the hydrocarbon products also resulted in an UCM in the gas chromatograms, with an increase in unresolved:resolved (U:R) component ratios from 0.1 to a maximum of 2.2 at 300 °C (Table 1).

The formation of pyrolysis products can be divided into three major compound classes: n-alkanes, stananes, and UCM, where the UCM decreases at temperatures >300 °C. There are some general trends recognizable. First, the overall oxidation products (mainly dehydrogenation) (e.g. PAHs, n-alkan-2-ones) increase in all experiments with increasing temperature above 200 °C. Second, reduction products increase with temperature (n-alkanes, stananes, Fig. 4), whereas cracking products (short chain alkanes, Diels’ hydrocarbon) increase at >350 °C (Table 1).

The yields of total alteration products obtained from sewage sludge biomass by hydrous pyrolysis with and without oxalic acid are illustrated in Fig. 4 and Table 1. The increasing concentrations are obvious as a function of temperature in both experiment sets, but the presence of oxalic acid clearly increased the yield by a factor of 1.44 ± 0.07. The conversion of sewage sludge increased with increasing temperature and acidity of the reaction mixture, indicating that pyrolysis under reducing conditions (with additional hydrogen) is more effective in converting sewage sludge OM to oil-like products.

The characteristics and yields of pyrolysis products of sewage sludge depend on feedstock, experimental conditions and the size and the type of the reactor [15,16,38,44–47]. Therefore, the final products and yields obtained by different investigators fluctuate. For example, pyrolysis of sewage sludge in a fixed bed reactor at 350–750 °C produced mainly oxygenated and nitrogenated aliphatic compounds with minor alicyclic and aromatic compounds [50]. The aromatic compounds increased with increasing temperature. Microwave oven pyrolysis of sewage sludge at 1000 °C showed a higher concentration of monoaromatics and 1-alkenes than alkanes [51]. It is obvious that the pyrolysis temperature and experimental conditions affect the yields, which vary from one experiment to another. The maximum yield was 52% at 450 °C [14], 30% at 525 °C [46], and 42.6% at 450 °C [52] when sewage sludge was heated in fluidized-bed reactors. For the microwave oven method at 650 °C and flash pyrolysis at 500 °C the maximum yields were 6% and 43.1%, respectively [52,53]. The yield was found to range from 10.7 wt.% to 67.5 wt.% when sewage sludge was heated over activated alumina at 450 °C [54]. Our results showed similar yields (Table 1), but at lower temperature (<400 °C).

**5. Conclusion**

The results of hydrous pyrolysis of sewage sludge show that the product yields increase with rising temperature in both the presence and absence of aqueous oxalic acid (in situ H2). The conversion rate increases by a factor of 1.4 with oxalic acid, indicating that pyrolysis under reducing conditions is more effective in converting sewage sludge OM to oil-like products. The concentrations of the various neutral compound groups (e.g. hydrocarbons) and UCM increase with rising temperature and longer reaction time to a maximum yield at 300–350 °C. Cracking and reformation reactions are obviously dominant at high temperatures (>300 °C). The data also show that: (1) the major products of hydrous pyrolysis are n-alkanes, stananes and UCM, (2) the oxygenated products

![Fig. 4. Concentration versus temperature plots for the yields of: (a) n-alkanoic acids, (b) n-alkanols, (c) steroids, (d) stananes, (e) Diels’ hydrocarbons, (f) n-alkanes, (g) UCM, and (h) total oil (closed circle = experiments with only water, open circle = experiments with oxalic acid).](image-url)
decrease with temperatures above 200 °C and (3) reduction products increase with temperature, competing with cracking reactions above 300 °C.

Acknowledgments

Financial support from the Distinguished Scientists Fellowship Program at King Saud University and the National Plan for Sciences and Technology (09-ENV658-02) is gratefully acknowledged.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2012.07.065.

References