Liquid fuels from sewage sludge through direct acid ethanolysis

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Outlook

- Chemical-characterization of sewage sludge
- Chemical exploitation of sewage sludge through ethanolysis
- Optimization of reactive conditions: fundamental study
- Valorization of sewage sludge through direct ethanolysis: feasibility study
- Conclusions
WWTPs

- Putignano: 190,000 PE
- Bari: 240,000 PE
- Barletta: 100,000 PE
- Lecce: 15,000 PE

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Primary Settling

Biological Oxidation

Sewage scum
Primary sludge
Secondary sludge
Mixed sludge

Biological Oxidation
Average values derived by analysis conducted on two different sample per WWTPs in two different period of the year.

EHS (Hemicellulose, Pectinic sugars, EPS)
Cellulose (Glucose, Xylose)
Lipids (Glycerides, Soaps, FFAs)
Proteins
HA&L
Ashes

>50% Organic Fraction
Lipids Characterization

<table>
<thead>
<tr>
<th></th>
<th>S Scum</th>
<th>PS</th>
<th>SS</th>
<th>MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Glycerides</td>
<td>16,8</td>
<td>0,4</td>
<td>42,9</td>
<td>1,4</td>
</tr>
<tr>
<td>% Soaps</td>
<td>23,9</td>
<td>90,3</td>
<td>0,0</td>
<td>88,9</td>
</tr>
<tr>
<td>% FFAs</td>
<td>59,3</td>
<td>9,3</td>
<td>57,1</td>
<td>9,7</td>
</tr>
</tbody>
</table>

Profile of FAs as «fingerprint» of different sewage sludge
Structural Sugars Characterization

Cellulose

EHS

IC-HPAED
1: Galactosamine
2: Arabinose
3: Glucosamine
4: Galactose
5: Glucose
6: Mannose + Xylose

Profiles of EHS as «fingerprint» of different sewage sludge
Reactions to be involved in valorization of sewage sludge

Furfural (F)

Glucose
Mannose
Galactose
Hexoses

Xylose
Ribose
Arabinose
Pentoses

Cellulose

Hemicellulose

FFAs
Soaps
Glycerides

Lipids

Ethyl Levulate (EL)

R: H, 5-Hydroxymethyl Furfural (HMF)
Et, 5-Ethoxymethyl Furfural (EMF)

FAEEs

Sewage Sludge

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Top Value Added Chemicals From Biomass

Volume I: Results of Screening for Potential Candidates from Sugars and Synthesis Gas

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<tr>
<td>3 hydroxy propionic acid</td>
<td></td>
</tr>
<tr>
<td>aspartic acid</td>
<td></td>
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<tr>
<td>glucaric acid</td>
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<td>glutamic acid</td>
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<td>3-hydroxybutyrolactone</td>
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</tr>
<tr>
<td>glycerol</td>
<td></td>
</tr>
<tr>
<td>sorbitol</td>
<td></td>
</tr>
<tr>
<td>xylitol/arabinol</td>
<td></td>
</tr>
</tbody>
</table>

As fuel, additive fuel, new materials...
Main objective:

To find out reactive conditions capable to convert sewage sludge components in a single step into the defined target molecules.
Lipid Valorization

Soaps

FFAs

Direct Esterification

FAEEs

Trans-Esterification

Glycerides

Acid Catalysis

60-80°C

2-4 h

Base or Acid Catalysis

60-80°C to 120-130°C

2-4 h to 10-12 h
Sugar Valorization

EHS

+ EtOH/H₂O, cat

1

Cellulose

Pentoses

Aldo-Hexoses

Brønsted acid Catalysed

Lewis acid Catalysed
A direct homogeneous Brønsted-Lewis acid catalysis was optimised

- Brønsted Acid: \( \text{H}_2\text{SO}_4 \)
- Lewis Acid: Aluminium and Iron salts were tested
- Operative Temperature: 180°C
- Reaction Time
### Ethanolysis of glucose

<table>
<thead>
<tr>
<th>E</th>
<th>Catalysts</th>
<th>G (%mol)</th>
<th>EG (%mol)</th>
<th>EF (%mol)</th>
<th>EMF +HMF (%mol)</th>
<th>EL (%mol)</th>
<th>Total (%mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Res.</td>
<td>Conv.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>No catalyst</td>
<td>74.9</td>
<td>25.1</td>
<td>13.1±0.6</td>
<td>6.9±0.4</td>
<td>0.2±0.1</td>
<td>20.2</td>
</tr>
<tr>
<td>2</td>
<td>H₂SO₄</td>
<td>3.5</td>
<td>96.5</td>
<td>65.6±1.2</td>
<td>1.3±0.2</td>
<td>1.8±0.2</td>
<td>27.6±0.8</td>
</tr>
<tr>
<td>3</td>
<td>AlCl₃·6H₂O</td>
<td>1.1</td>
<td>98.9</td>
<td>48.3±0.9</td>
<td>1.2±0.2</td>
<td>27.1±0.7</td>
<td>17.1±0.3</td>
</tr>
<tr>
<td>4</td>
<td>FeCl₃·6H₂O</td>
<td>10.4</td>
<td>89.6</td>
<td>85.8±1.1</td>
<td>2.4±0.2</td>
<td>6.1±0.2</td>
<td>0.7±0.2</td>
</tr>
</tbody>
</table>

Al salts were found more active than respective Fe salts.

In the case of AlCl₃·6H₂O (30%mol respect to G) a synergic effect with H₂SO₄ was obtained.

After only 2 h, about 60% of starting glucose was converted into EL+HMF+EMF.

Reactive conditions: 180°C, 2h.
Ethanolysis of simple sugars

Besides EL, HMF and EMF, EG were mostly obtained.

Ethanolysis occurred efficiently on all sugars and amino-sugars.

Reactive conditions: 180°C, 2h
Ethanolysis of simple sugars: effect of water

- Solubilization of starting sugars was obtained
- EGs represent the main products

Reactive conditions: 180°C, 2h
Ethanolysis of complex sugars

**Glucose**

![Graph showing ethanolysis of Glucose over time]

**Starch**

![Graph showing ethanolysis of Starch over time]

**Reaction time: 6 h**
Ethanolysis of Sewage Sludge (1)

**Materials and Methods**

1. **Sludge**
2. **Ethanol**
3. **6h, 180°C**

**Characterization**

- GC-FID
- GC-MS
- IC-HPAED
- Derivatization

**Evaluation of RS**
# Ethanolysis of Sewage Sludge (2)

<table>
<thead>
<tr>
<th>Sludge</th>
<th>Lipid Conversion</th>
<th>Carbohydrates Conversion</th>
<th>Yield of EL</th>
<th>Yield of HMF+EMF</th>
<th>Yield of F</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%wt</td>
<td>%wt</td>
<td>%m*</td>
<td>%m*</td>
<td>%m**</td>
</tr>
<tr>
<td>Sewage scum</td>
<td>&gt;99</td>
<td>65</td>
<td>42</td>
<td>10</td>
<td>78</td>
</tr>
<tr>
<td>Primary</td>
<td>&gt;99</td>
<td>55-60</td>
<td>32</td>
<td>8</td>
<td>80</td>
</tr>
<tr>
<td>Secondary</td>
<td>&gt;99</td>
<td>99</td>
<td>45</td>
<td>12</td>
<td>82</td>
</tr>
<tr>
<td>Mixed</td>
<td>&gt;99</td>
<td>75</td>
<td>36</td>
<td>8</td>
<td>81</td>
</tr>
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</table>

\[
Yield \, (\%) = \frac{n \text{ mole of product (experimental)}}{n \text{ mole of product (theoretical)}} \times 100
\]

Results were congruent with RS analysis: EHS, proteins and lipids were completely absent. Cellulose was present in traces and with a different profile: no xylose was found.
Ethanolysis of Sewage Sludge (3)

Mixed Sludge

EL, HMF and EMF

FAEEs (Biodiesel)

EHS
Cellulose
Lipids
Proteins
HA&L
Ashes

RS

Dry conditions

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Fine chemicals and new materials
Ethanolysis of Sewage Sludge (4)

Mixed Sludge

In presence of water

RS
(partial content of cellulose)

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Ethanolysis of Sewage Sludge (5)

1 Tonn (as dewatered sludge)

20-25 MJ/Kg_{ST}

- Ethanol
- 6h, 180°C
- RS (45% of starting sludge)
- 70 Kg of Dry Residual Solids
- HA&L (25%)
- EGs
- HMF-EMF
- Aminoacids
- FAEEs
- 30-35 MJ/Kg_{ST}

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Conclusions

Direct ethanolysis of sewage sludge was investigated. Through a combined Brønsted-Lewis acid ethanolysis, the following main points were achieved:

1. Structural carbohydrates were mainly converted into EL, HMF and EMF under dry conditions, in EGs in presence of water
2. Lipids were always efficiently converted in FAEEs (namely biodiesel): potentially such a process could satisfy about the 20% of the present European Demand of Biodiesel
3. Proteins were also hydrolised and aminoacids were ethyl-esterified and preserved in solution by thermal degradation
4. Residual Solids resulted significantly reduced
Aknowledgements

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Sandro Menegatti
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Thank you for your kind attention!