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


AUSTRIA
SWITZERLAND
HUNGARY
SLOVENIA
CROATIA
BOSNIA - HERZEGOVINA
FRANCE
MONACO
SAN MARINO
VATICAN CITY
ITALY
Adriatic Sea
Tyrrhenian Sea
Mediterranean Sea
Ionian Sea
Gulfo di Taranto
CORSICA
SARDINIA
SICILY
TUNISIA
ALGERIA
Rome
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Taranto
Naples
Milan
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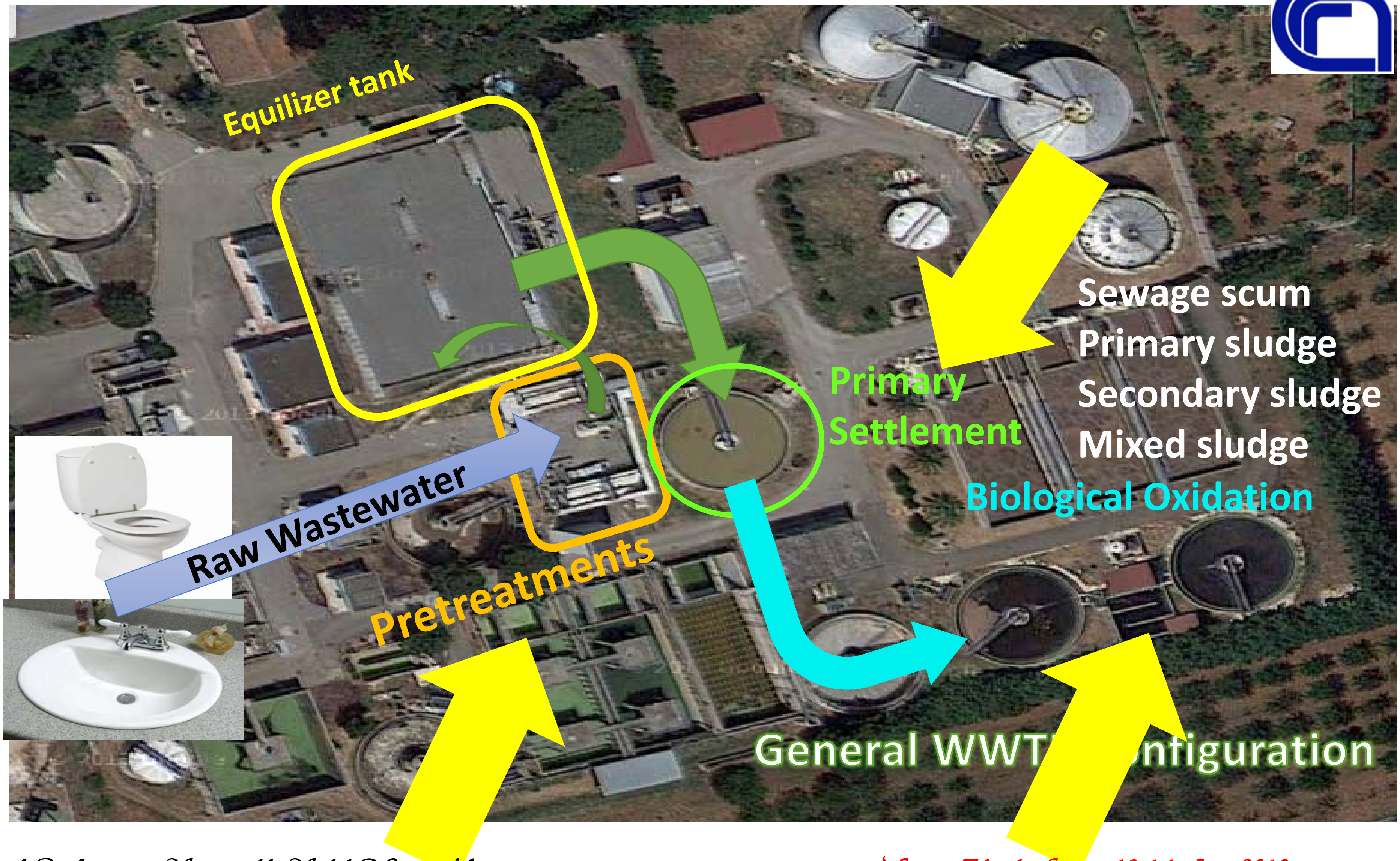
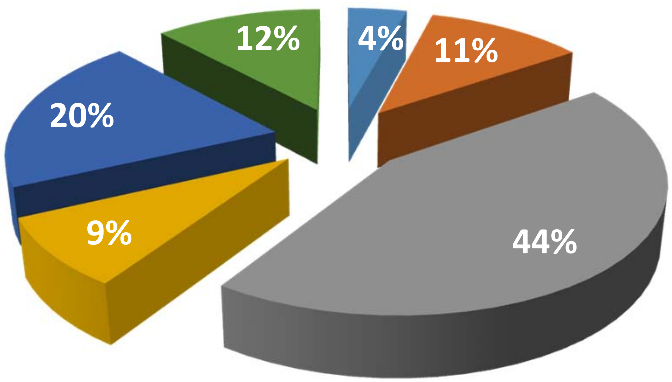
PE 100.000
Barletta
PE 240.000
Bari
PE 15.000
Putignano
PE 190.000
Lecce
Manfredonia
Foggia
Andria
Polignano A Mare
Monopoli
Altamura
Matera
Ostuni
Brindisi
Taranto
Potenza
Melfi
Sala Consilina
Policoro
Porto Cesareo
A14
E842
E843
E90
E847

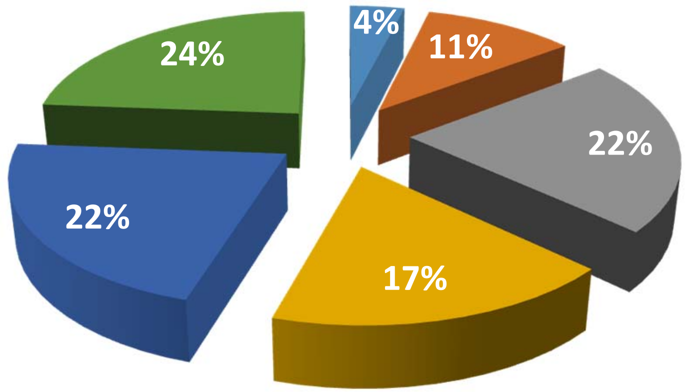


Equilizer tank
Primary
Settlement
Sewage scum
Primary sludge
Secondary sludge
Mixed sludge
Biological Oxidation
Raw Wastewater
Pretreatments
General WWT
nfiguration

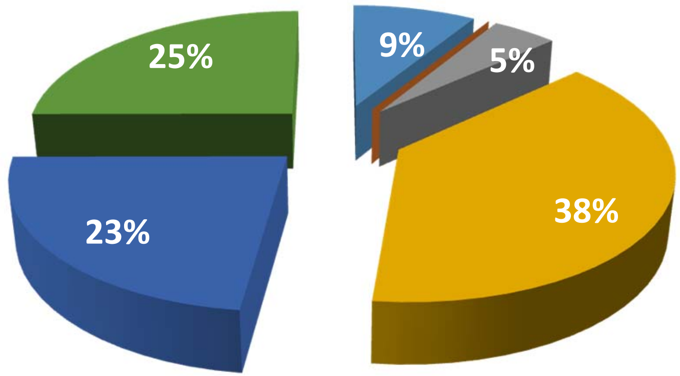
Sewage Scum



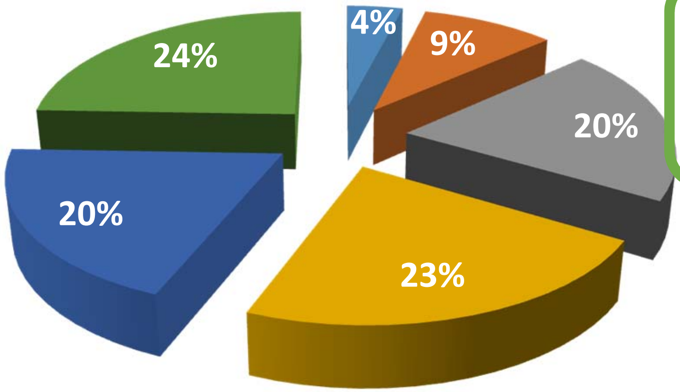
Primary Sludge



Secondary Sludge



Mixed Sludge



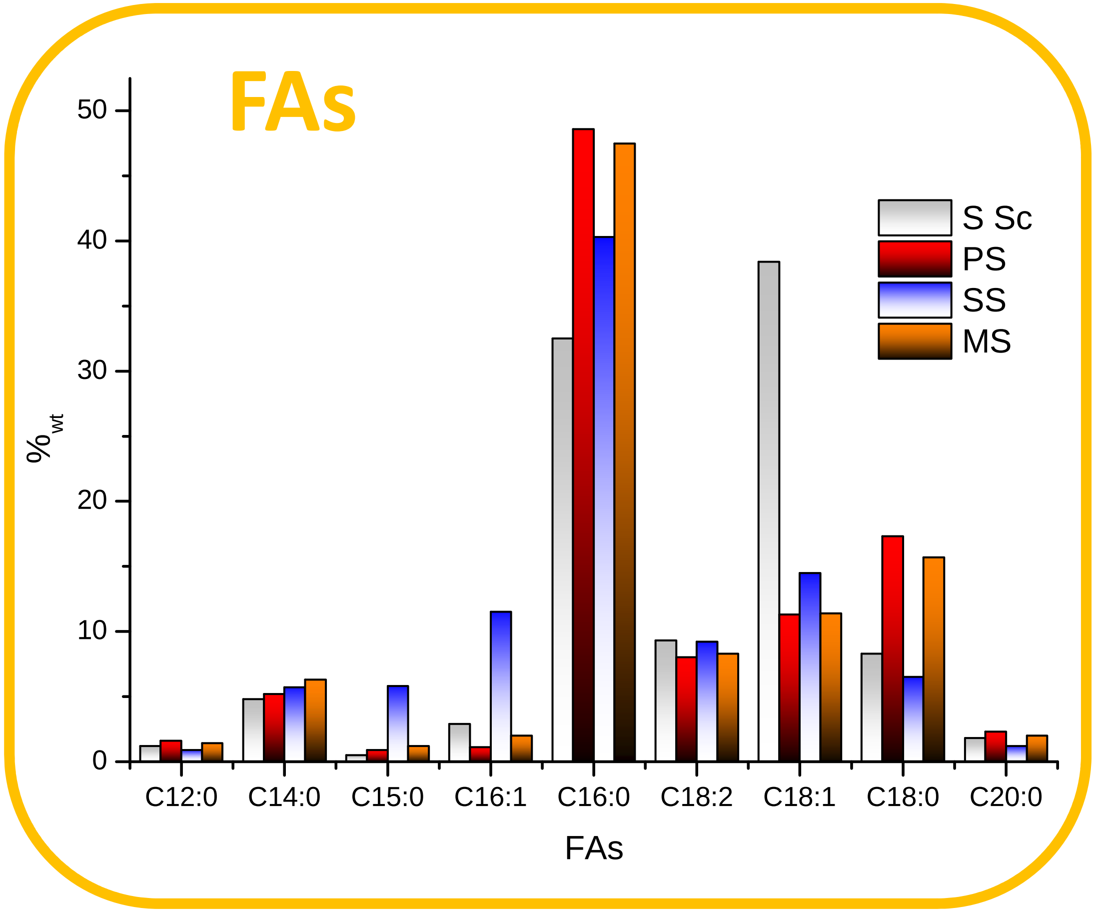
- EHS (Hemicellulose, Pectinic sugars, EPS)
- Cellulose (Glucose, Xylose)
- Lipids (Glycerides, Soaps, FFAs)
- Proteins
- HA&L
- Ashes

>50% Organic Fraction

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

Lipids Characterization

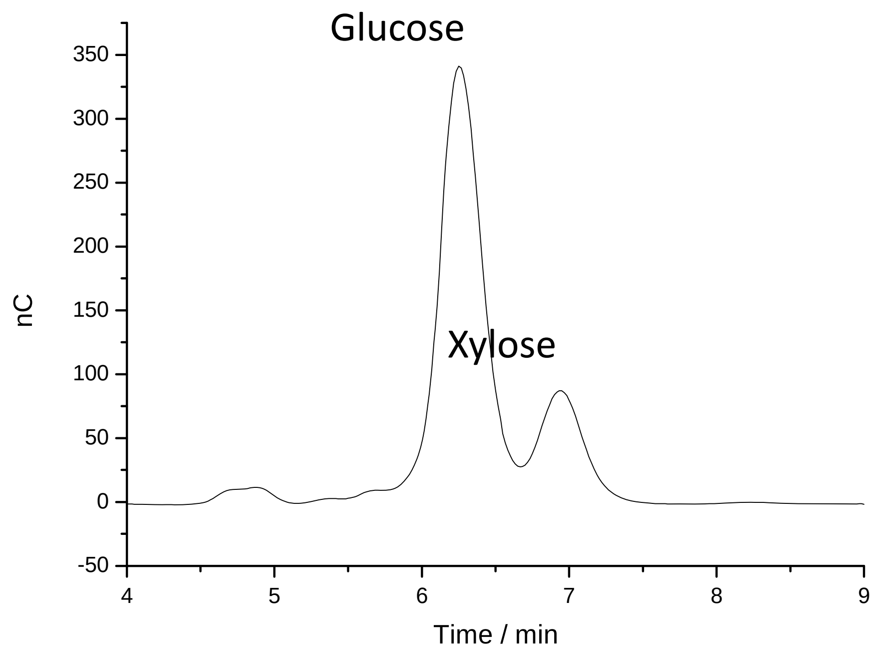
	S Scum	PS	SS	MS
	%	%	%	%
Glycerides	16,8	0,4	42,9	1,4
Soaps	23,9	90,3	0,0	88,9
FFAs	59,3	9,3	57,1	9,7



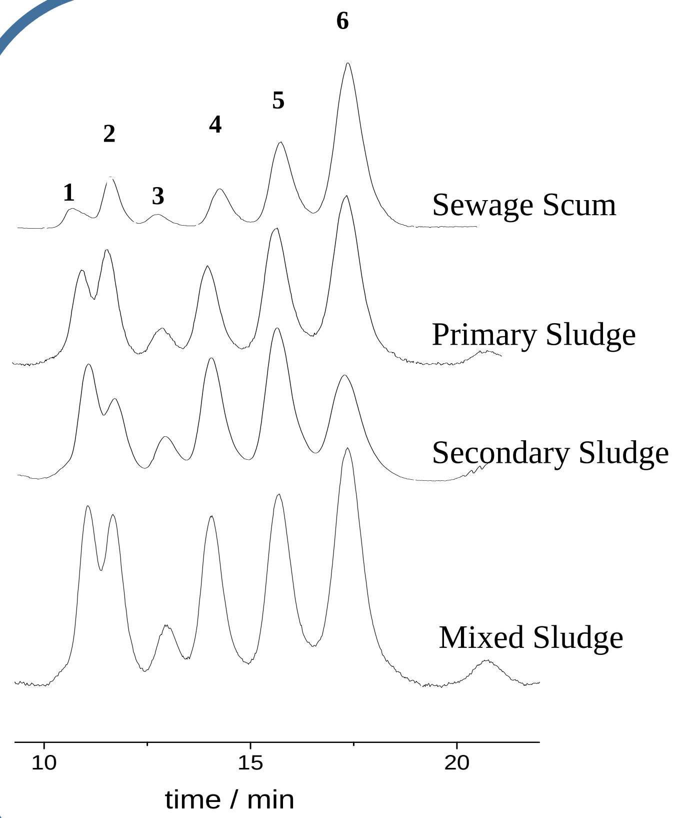
Profile of FAs as «fingerprint» of different sewage sludge

Structural Sugars Characterization

Cellulose



EHS

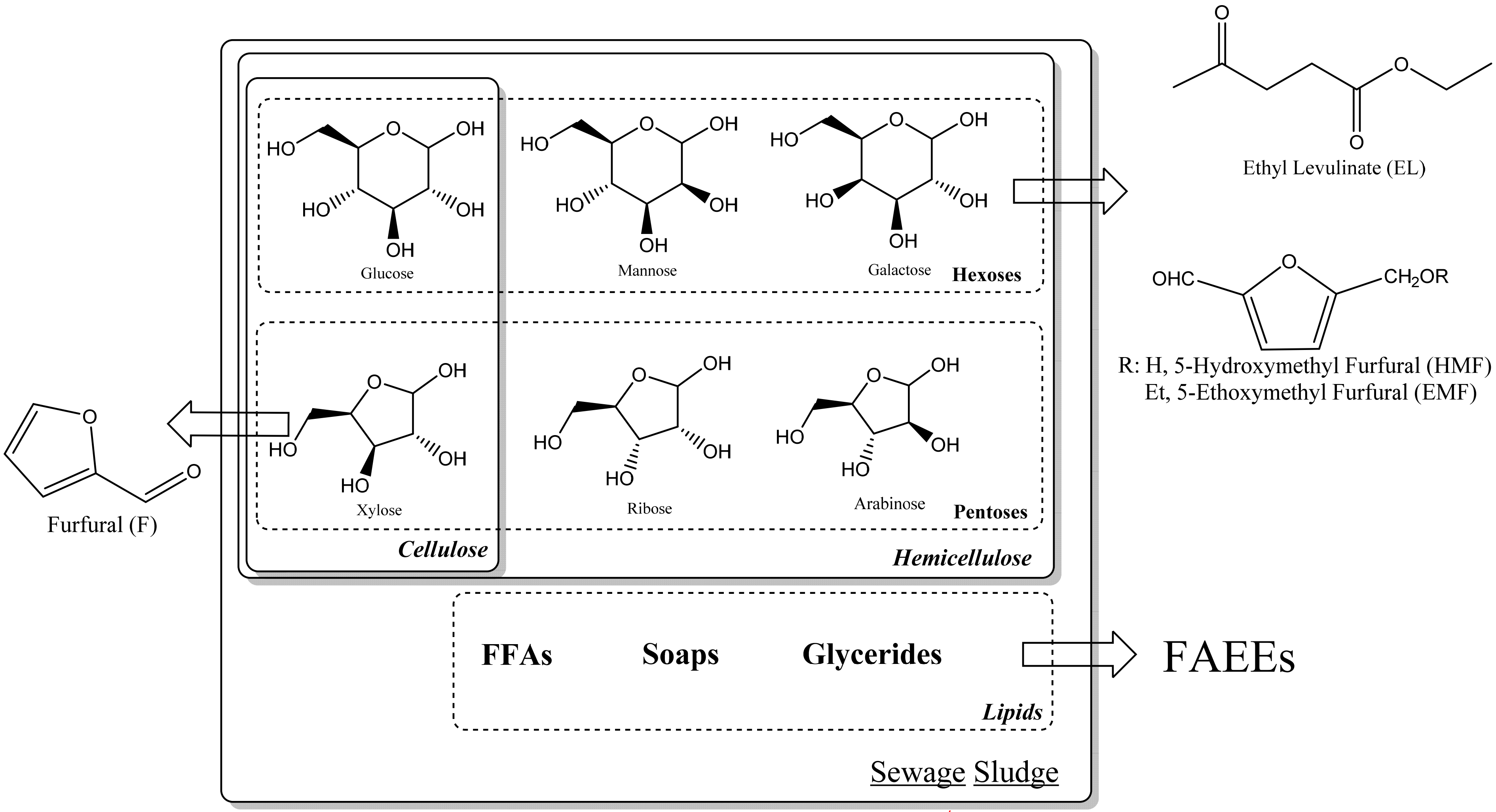


IC-HPAED

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



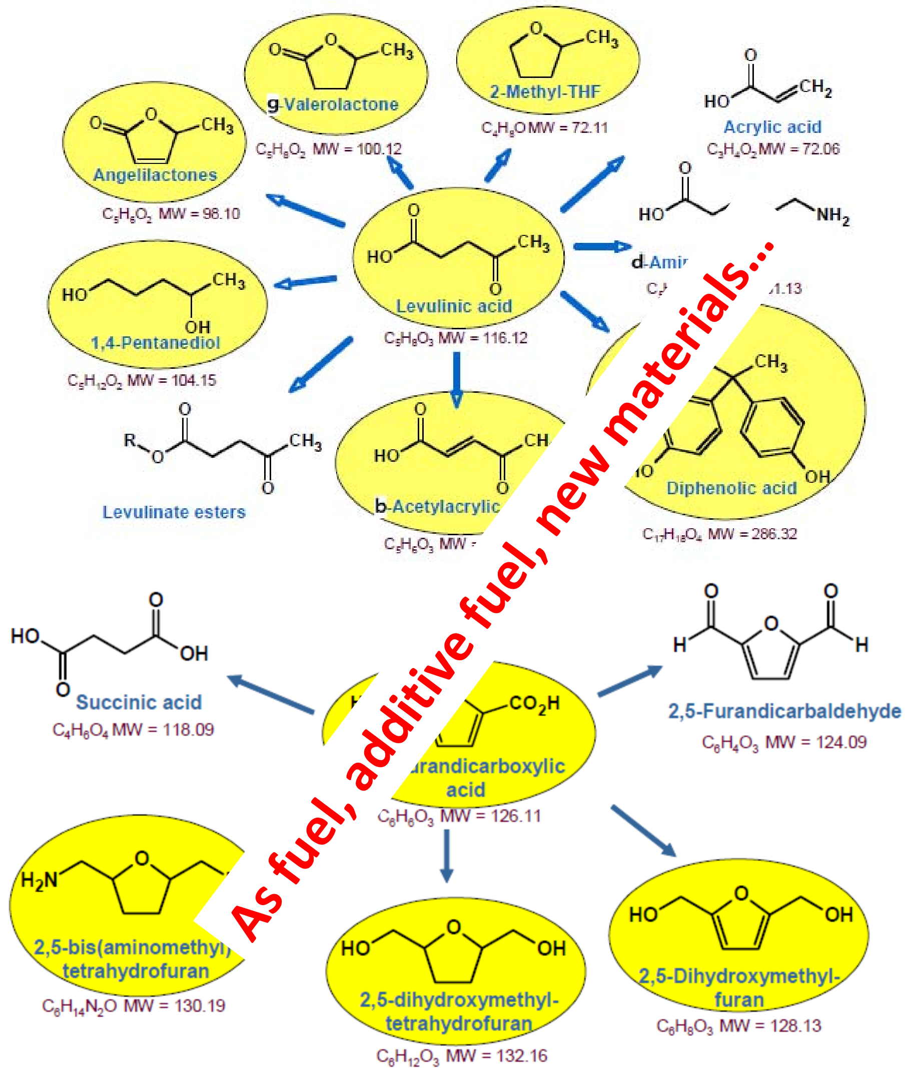
National Renewable Energy Laboratory

Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy

Top Value Added Chemicals From Biomass

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

Building Blocks
1,4 succinic, fumaric and malic acids
2,5 furan dicarboxylic acid
3 hydroxy propionic acid
aspartic acid
glucaric acid
glutamic acid
itaconic acid
levulinic acid
3-hydroxybutyrolactone
glycerol
sorbitol
xylitol/arabinitol



Main objective:

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

Lipid Valorization

Soaps

FFAs

Direct Esterification →

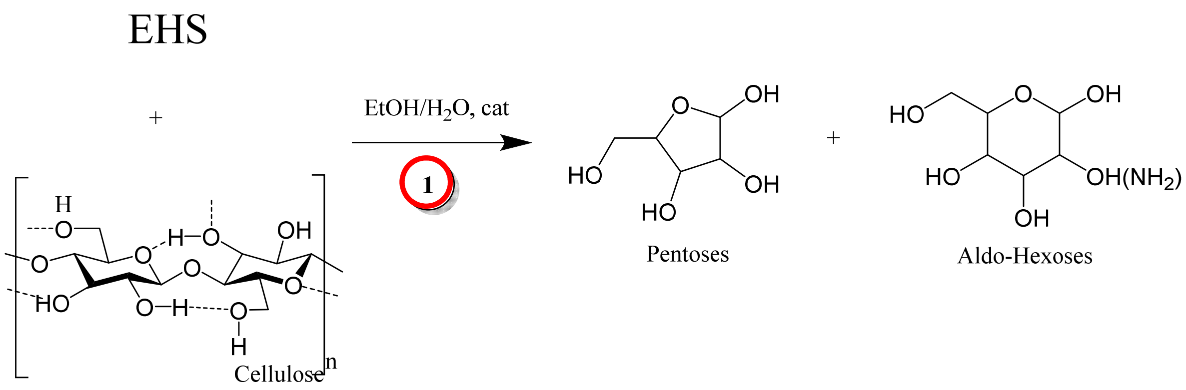
FAEEs

← Trans-Esterification

Glycerides

Direct Esterification	Trans-Esterification
Acid Catalysis	Base or Acid Catalysis
60-80°C	60-80°C to 120-130°C
2-4 h	2-4 h to 10-12 h

Sugar Valorization

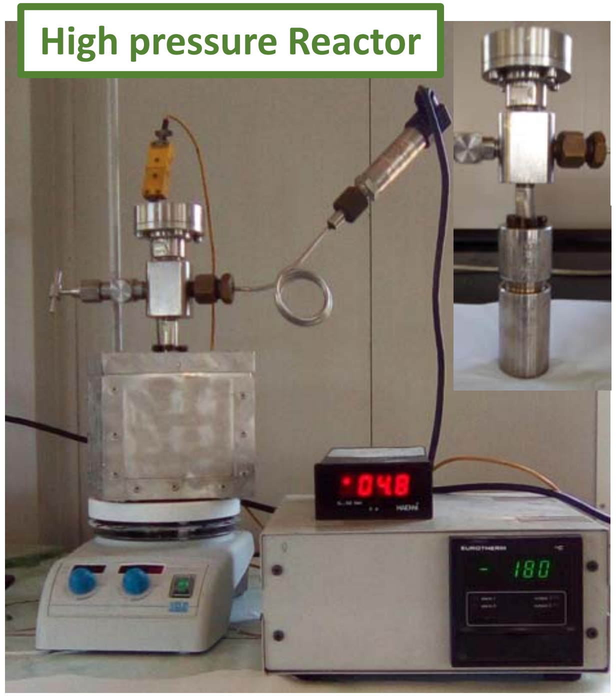


○ : Brønsted acid Catalysed

○ : Lewis acid Catalysed

A direct homogeneous Brønsted-Lewis acid catalysis was optimised

- **Brønsted Acid: H_2SO_4**
- **Lewis Acid: Aluminium and Iron salts were tested**
- **Operative Temperature: 180°C**
- **Reaction Time**



Ethanolysis of glucose

E	Catalysts	G (%mol)		EG (%mol)	EF (%mol)	EMF +HMF (%mol)	EL (%mol)	Total (%mol)
		Res.	Conv.					
1	No catalyst	74.9	25.1	13.1±0.6	6.9±0.4	0.2±0.1	-	20.2
2	H_2SO_4	3.5	96.5	65.6±1.2	1.3±0.2	1.8±0.2	27.6±0.8	96.3
3	$AlCl_3{\cdot}6H_2O$	1.1	98.9	48.3±0.9	1.2±0.2	27.1±0.7	17.1±0.3	93.7
4	$FeCl_3{\cdot}6H_2O$	10.4	89.6	85.8±1.1	2.4±0.2	6.1±0.2	0.7±0.2	95.0

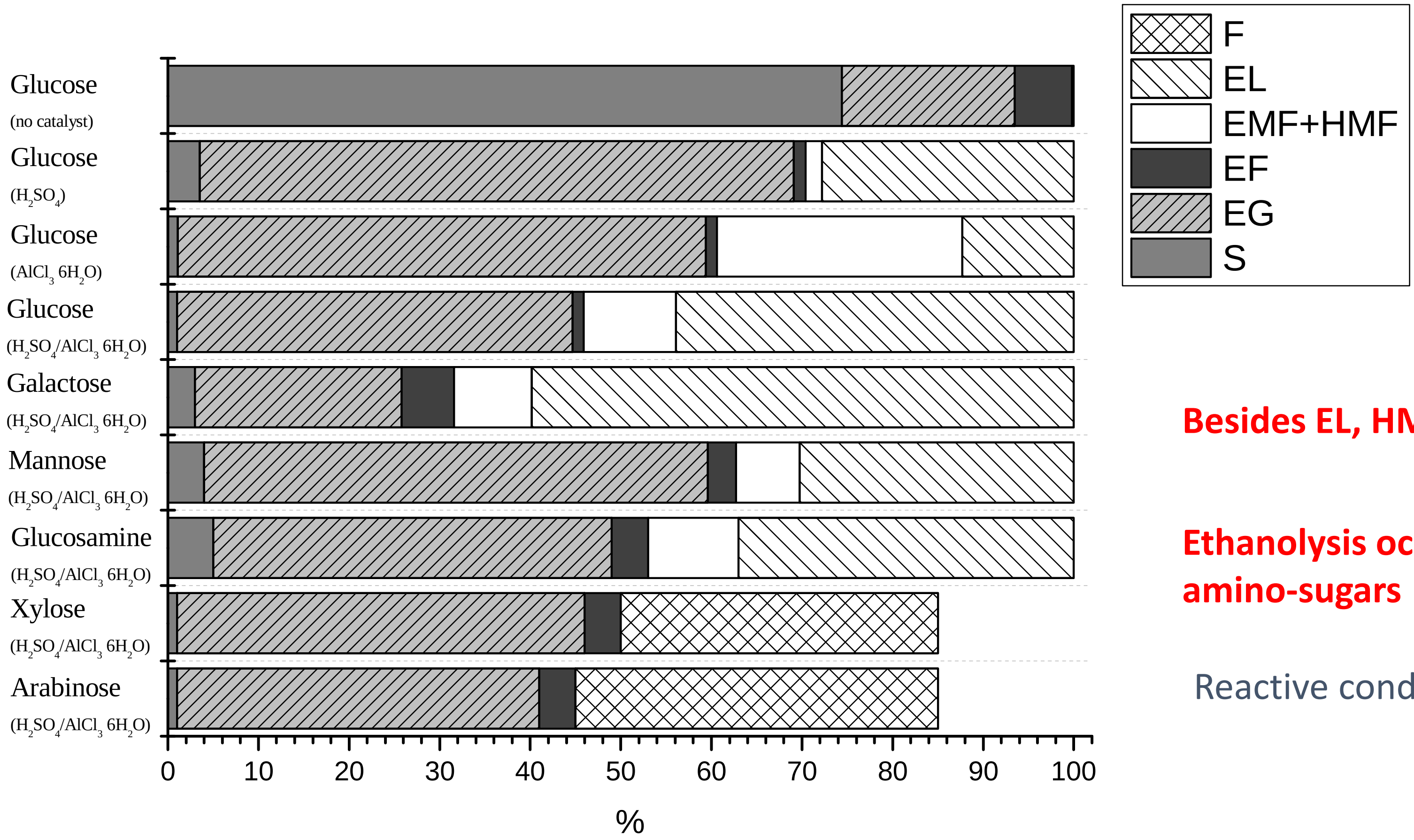
Al salts were found more active than respective Fe salts

In the case of $AlCl_3{\cdot}6H_2O$ (30%mol respect to G) a synergic effect with H_2SO_4 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

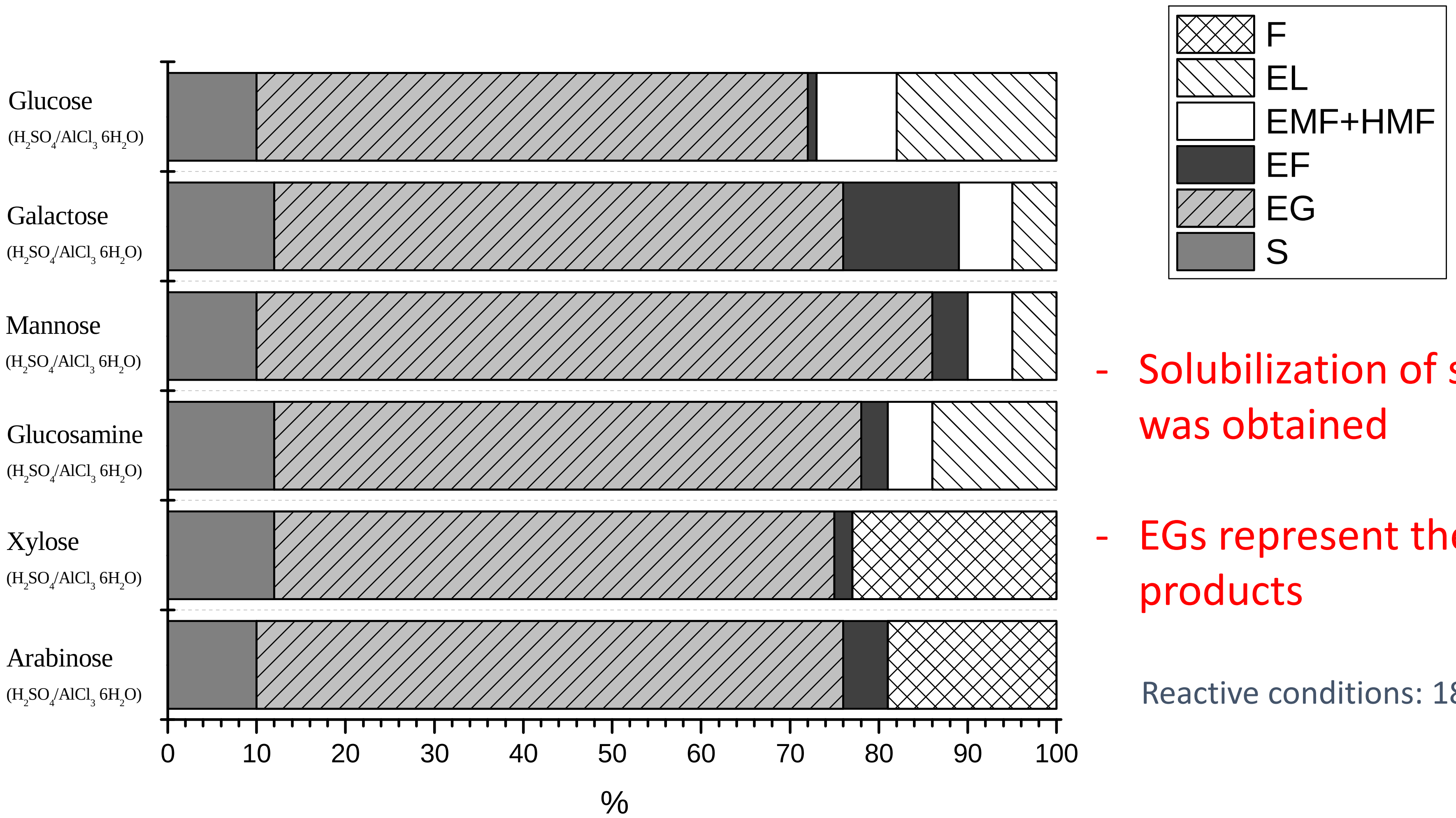


Besides EL, HMF and EMF, EG were mostly obtained

Ethanolysis occurred efficiently on all sugars and amino-sugars

Reactive conditions: 180°C, 2h

Ethanolysis of simple sugars: effect of water

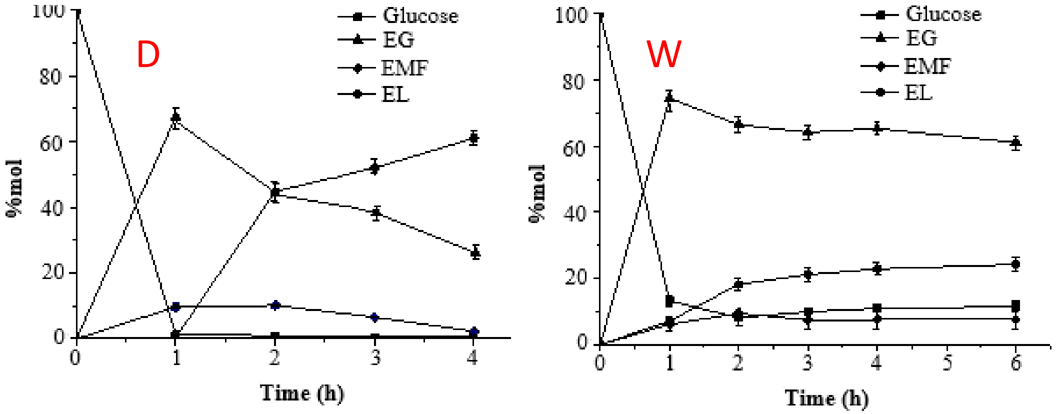


- Solubilization of starting sugars was obtained
- EGs represent the main products

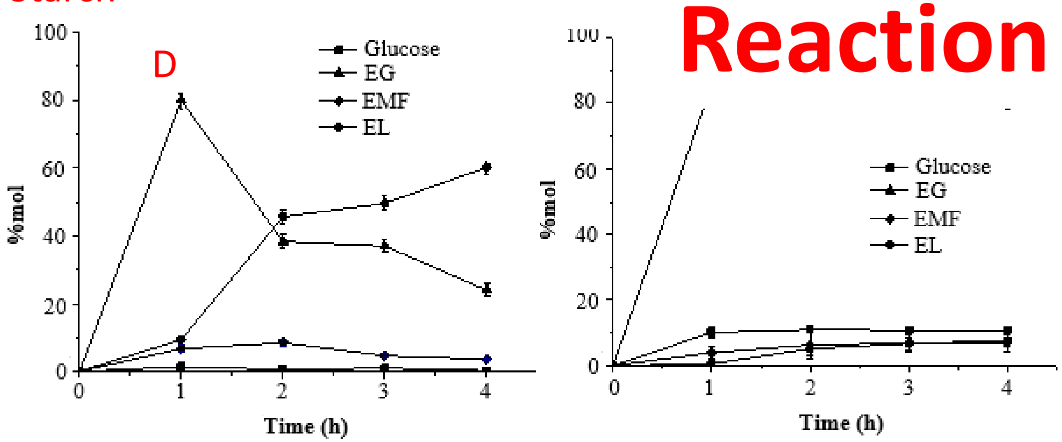
Reactive conditions: 180°C, 2h

Ethanolysis of complex sugars

Glucose



Starch



Reaction time: 6 h

Ethanolysis of Sewage Sludge (1)

Ethanol

6h, 180°C

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

Evaluation of RS

Characterization

Ethanolysis of Sewage Sludge (2)

Sludge	Lipid Conversion	Carbohydrates Conversion	Yield of EL	Yield of HMF+EMF	Yield of F
	%wt	%wt	%m*	%m*	%m**
Sewage scum	>99	65	42	10	78
Primary	>99	55-60	32	8	80
Secondary	>99	99	45	12	82
Mixed	>99	75	36	8	81

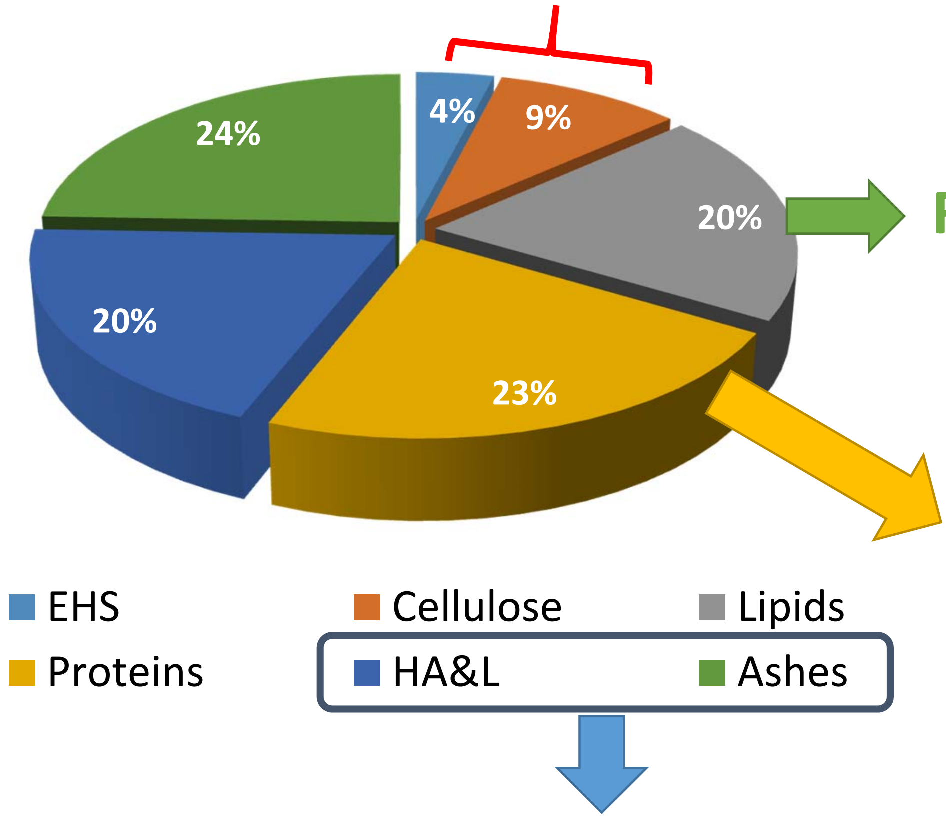
$$Yield\ (\%) = \frac{n\ mole\ of\ product\ (experimental)}{n\ mole\ of\ product\ (theoretical)} * 100$$

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.

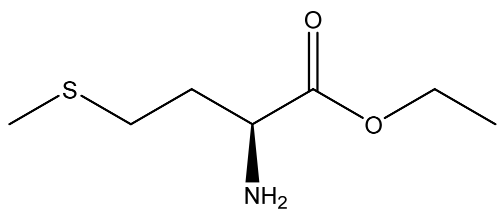
Ethanolysis of Sewage Sludge (3)

Mixed Sludge

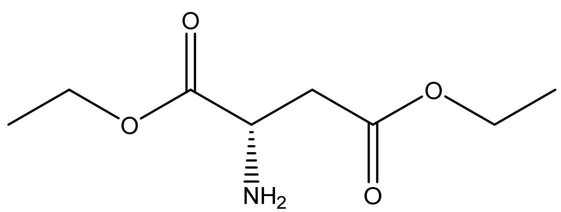
Dry conditions



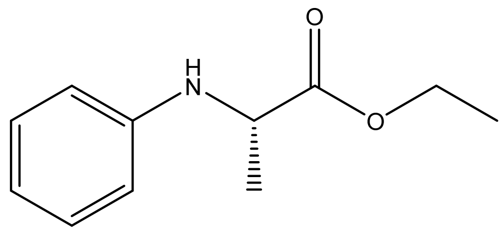
FAEEs (Biodiesel)



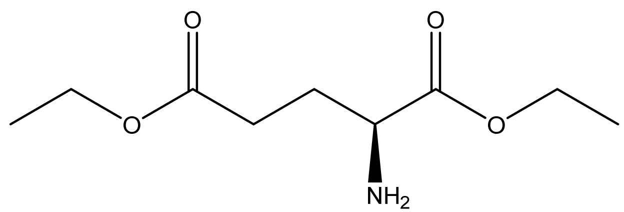
Methionine ethyl ester



Aspartic acid di-ethyl ester



Phenyl alanine ethyl ester



Glutamic acid di-ethyl ester

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glucaric acid
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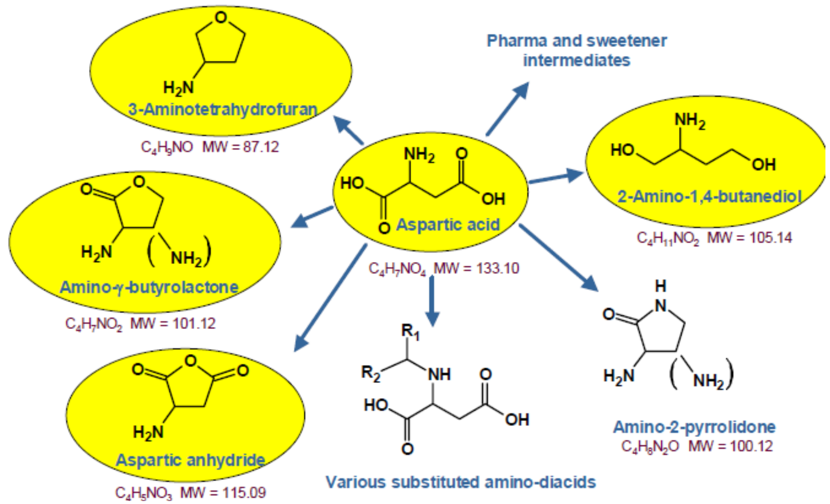
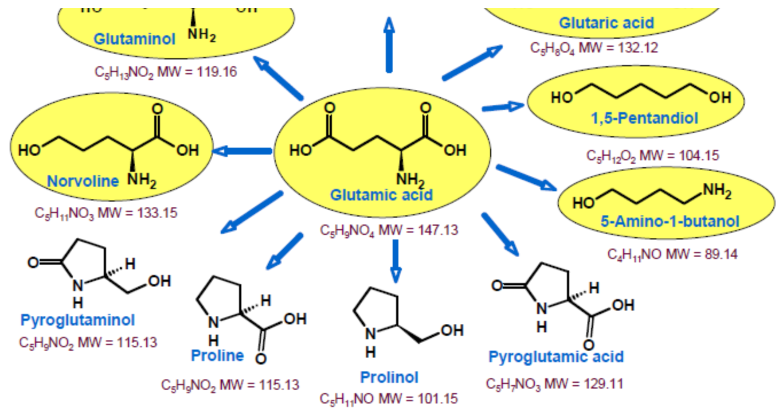
itaconic acid
levulinic acid
3-hydroxybutyrolactone
glycerol
sorbitol
xylitol/arabinitol

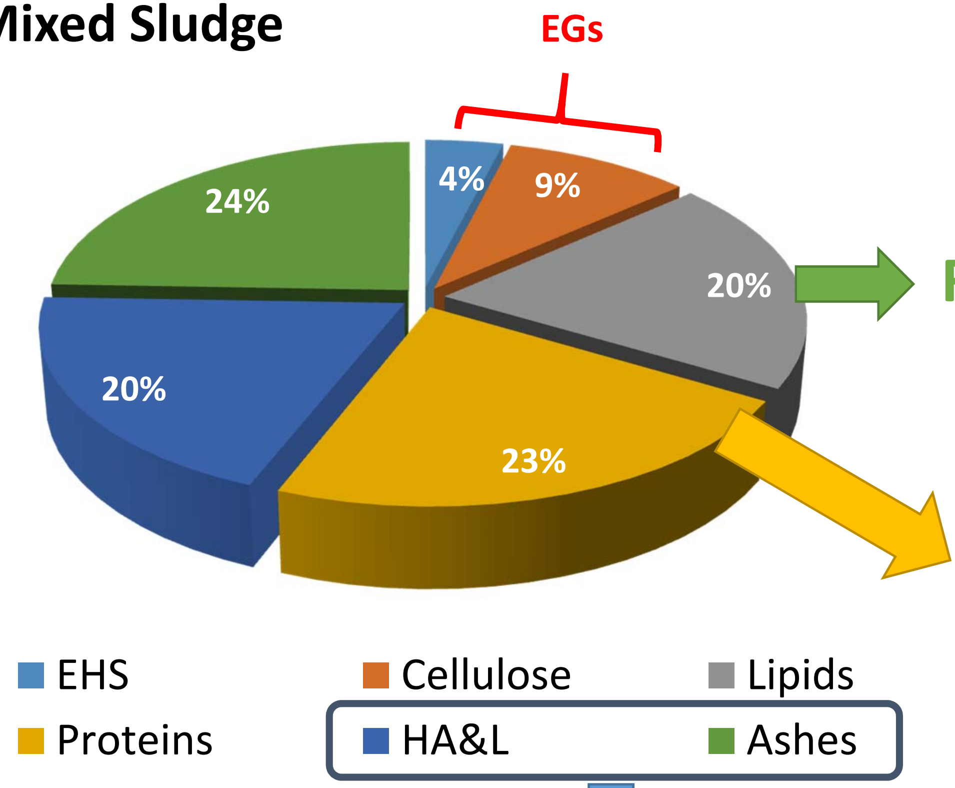


Fine chemicals and new materials



Ethanolysis of Sewage Sludge (4)

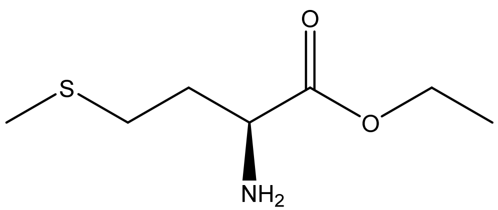
Mixed Sludge



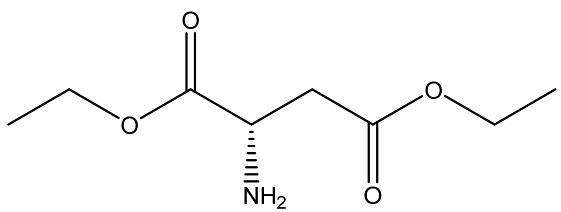
RS

(partial content of cellulose)

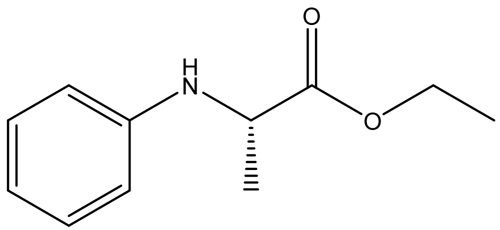
In presence of water



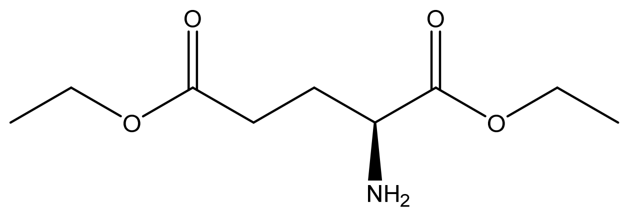
Methionine ethyl ester



Aspartic acid di-ethyl ester



Phenyl alanine ethyl ester



Glutamic acid di-ethyl ester

Ethanolysis of Sewage Sludge (5)

1 Tonn
(as dewatered sludge)

20-25 MJ/Kg$_{ST}$

Ethanol

6h, 180°C

- **EGs**
- **HMF-EMF**
- **Aminoacids**
- **FAEEs**

30-35 MJ/Kg$_{ST}$

RS (45% of starting sludge)

70 Kg of Dry Residual Solids

HA&L (25%)

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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acquedotto pugliese

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Thank you for your kind attention!