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PRELIMINARY STUDY AMONG CONVENTIONAL PYROLYSIS AND CATALYTIC PYROLYSIS OF SEWAGE SLUDGE

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Bioenergy III: Present and New Perspectives on Biorefineries
Lanzarote (Spain), May 24th, 2011

Outline

- **Introduction and Objectives**
- **Materials and Methods**
- **Results:**
  - Product yields
  - Organic and aqueous phase yields
  - Elemental composition of organic phases
  - Organic phase properties: relation O/C, H/C, HHV
- **Conclusions**

Outline

- Introduction and Objectives

Introduction and objectives

- The number of wastewater treatment plants has increased during the last years, due to the strict legislation (Directive 91/271/EEC).

It is necessary to find alternatives for management and valorization of sewage sludge

Thermochemical processing of sewage sludge via pyrolysis comes up as an interesting alternative

Introduction and objectives

- In previous studies (*), pyrolysis of sewage sludge in a fluidized bed yielded a liquid fraction with two organic phases and an aqueous one.
- The organic phases contain a significant amount of triglycerides and fatty acids:
  - high contribution to the heating value of the liquids
  - Viscosity and oxygen content are increased.
- γ-Al_2O_3 catalysts have shown a good performance in the decarboxylation of triglycerides and fatty acids (**,***)

* Fonts. I, Juan.A, Gea.G, Murillo.M.B, Sánchez. J. L., Ind. Eng. Chem. Res. 47 (2008) 5376-5385

** Konar. S.K, Boocock, D.G.B., Mao, V., Liu, J., Fuel 73 (1994) 642-646

*** Vonghia.E, Boocock, D.G.B., Konar, S.K., Leung, A., Energy Fuels, 9 (1995)

Introduction and objectives

Main objective:

To improve the properties of the sewage sludge pyrolysis liquid by means of an in-situ catalytic treatment

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Materials and methods

Raw material:

- Anaerobically digested and dried sewage sludge supplied by a Spanish wastewater treatment plant (Madrid Sur (SSM)).
- Particle size: -500 +250 μm

Dried sewage sludge

Feedstock analyses

Elemental analysis		Moisture	Ash	Volatiles	Fixed Carbon
		ISO-589-1981	ISO-1171-1976	ISO-5623-1974	By difference
wt % units		7.1	41.0	46.6	5.3
Ultimate analysis	C	H	N	S	O
	ASTM D 5373	ASTM D 5373	ASTM D 5373	ASTM D 4239	By difference
wt % units	27.7	4.4	3.9	0.8	22.2

[a] The wt-% of hydrogen includes the hydrogen from moisture.

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Materials and methods

Catalyst:

- Activated γ-Al_2O_3
  - Calcined at 600 ºC
  - Surface area (BET): 142 m^2/g
  - Average pore size: 10.5 nm
  - Volume of mesopores (BJH): 0.4 cm^3/g

γ-Al_2O_3 chemical composition

Compound	wt %
Al_2O_3	95.0 min
C	0.05 max
SiO_2	0.035 max
Fe_2O_3	0.025 max
Na_2O	0.005 max
TiO_2	0.27 max

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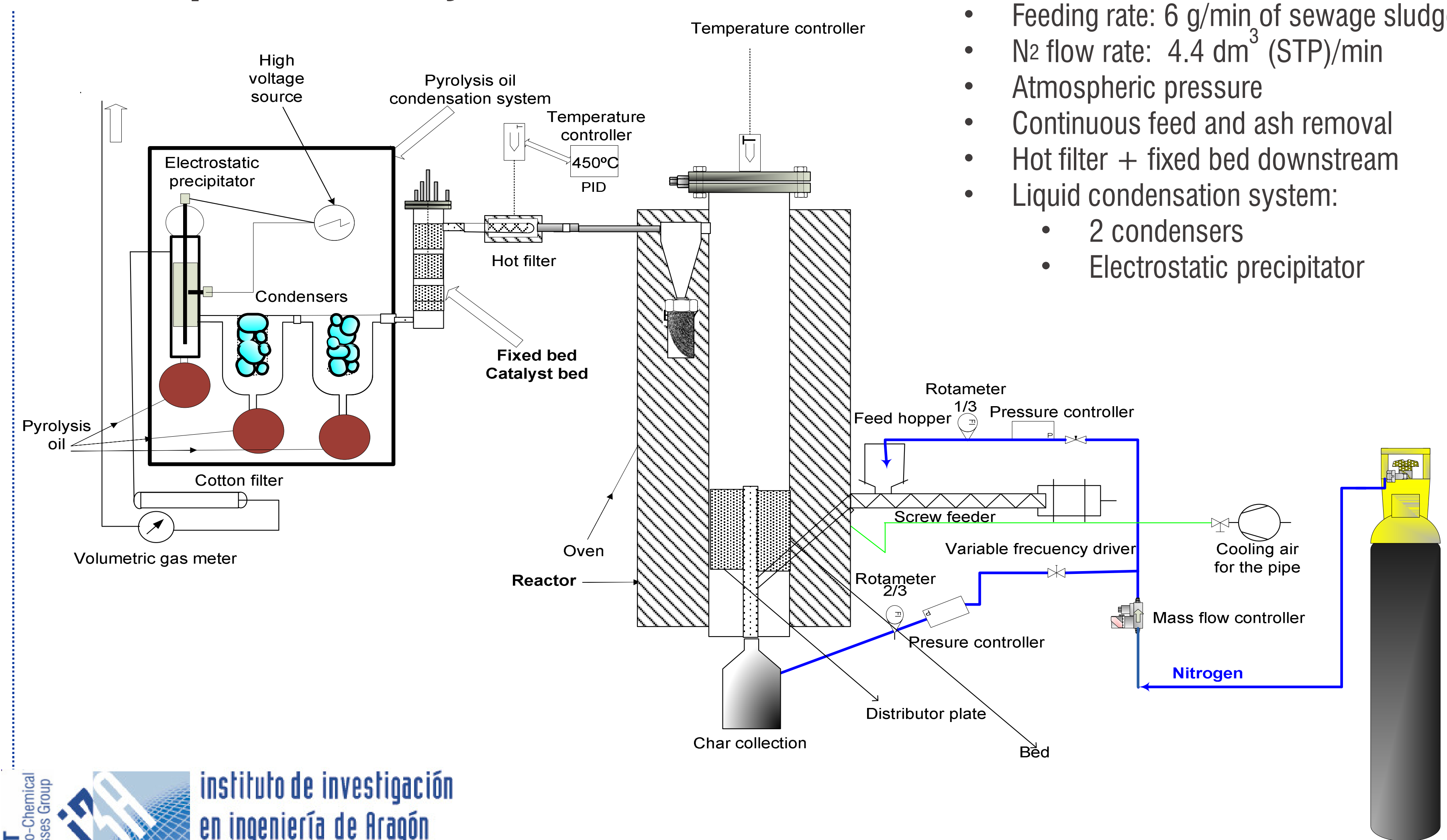
Materials and methods

Experimental system:



- Lab-scale fluidized bed (< 1 kg/h)
- Feeding rate: 6 g/min of sewage sludge
- N_2 flow rate: 4.4 dm^3 (STP)/min
- Atmospheric pressure
- Continuous feed and ash removal
- Hot filter + fixed bed downstream
- Liquid condensation system:
  - 2 condensers
  - Electrostatic precipitator

Materials and methods

Experimental conditions:

Bed constituent	Inert Sand	γ-Alumina	
Experiment number	**1**	**2**	**3**
Bed temperature fluidized bed reactor (ºC)	550	550	550
Freeboard temperature (ºC)	450	450	450
Temperature fixed bed (ºC)	500	500	500
Gas residence time FBR (s)	1.2	1.2	1.2
Height of catalytic bed (cm)	0	5	10
Amount of catalyst (g)	0	97	194
WHSV (vapour mass flow/mass catalyst) (h^{-1})		1.7	0.8
Run time (min)	120	120	120

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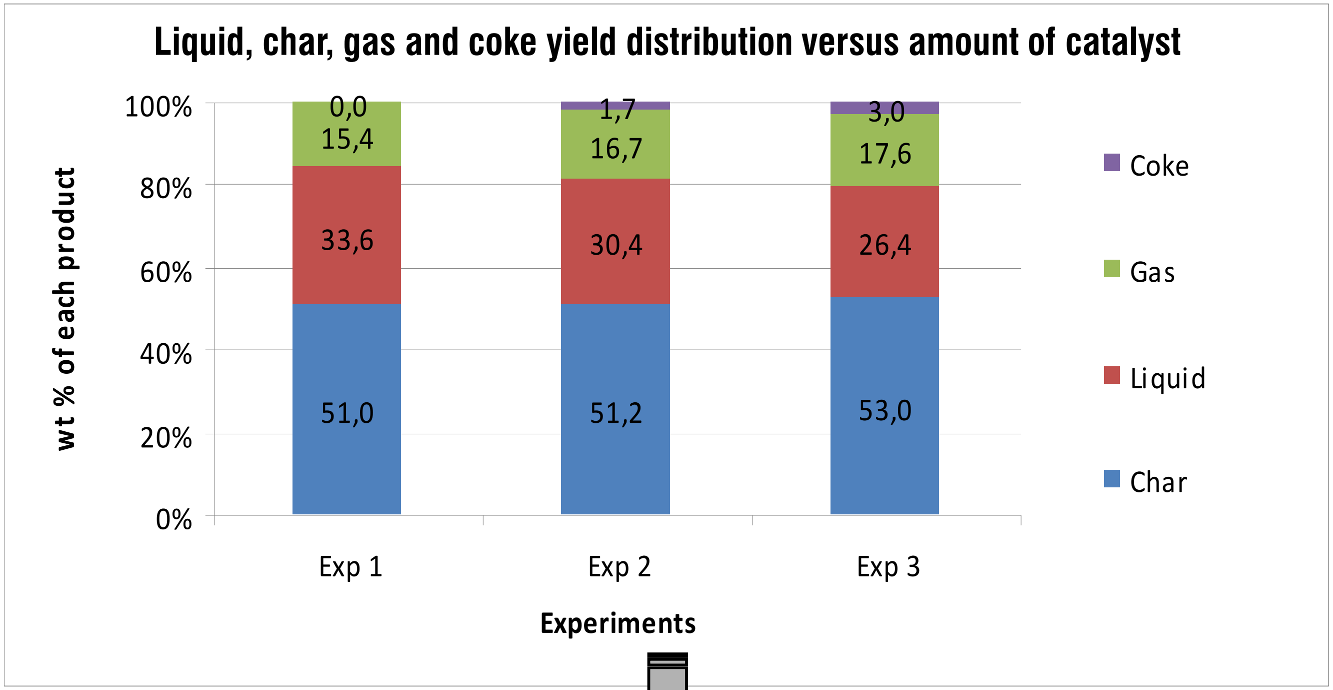
Results

Product yields:

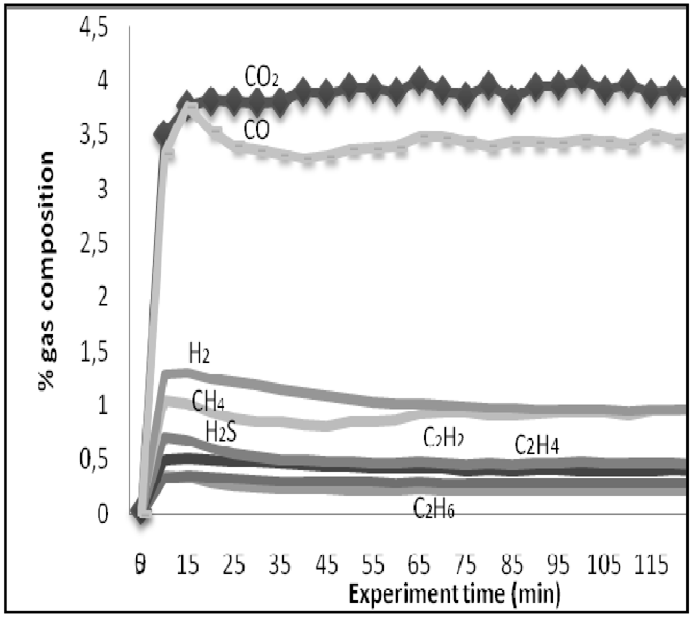


Gas yield increases when the catalyst load becomes increased
Liquid yield becomes decreased
Low deposition of coke on the catalyst

Results

Product yields:

Gas composition during experiment 2 (Fluid. bed: 550 ºC, Fixed bed: 500 ºC, 97g γ-Al_2O_3).



Gas composition remained constant throughout

The product gases were CO, CO_2, H_2, C_2H_2, C_2H_4 and C_2H_6

The presence of γ-Al_2O_3 did not significantly alter the gas composition

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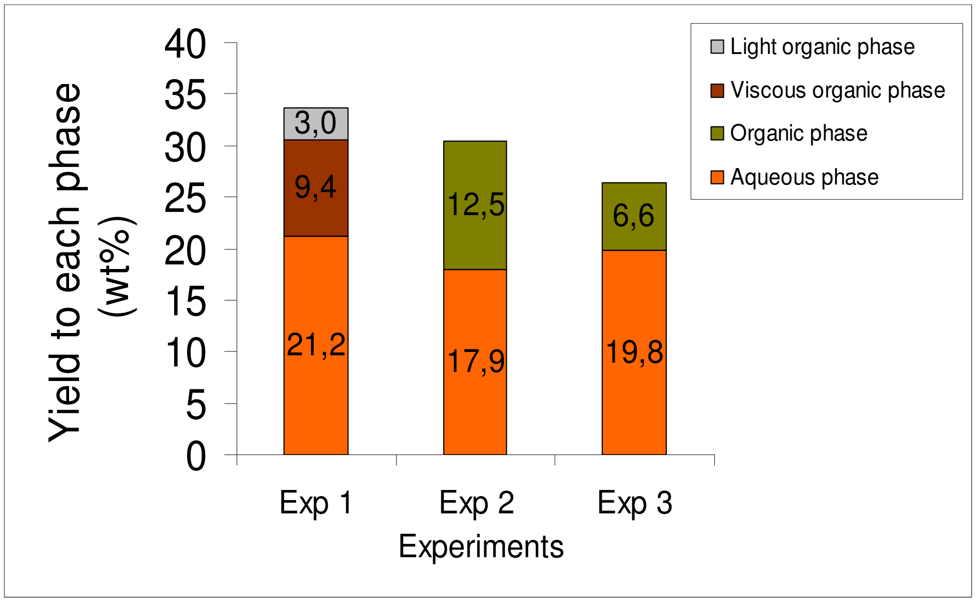
Results

Liquid physicochemical properties:

Liquid yield and phase distribution versus amount of catalyst



Inert sand → Three phases

γ-Al_2O_3: Only two phases of different colours → easier separation.

The organic fraction yield, decreased with the highest catalyst load, and the HHV increased.

Organic phase obtained (Exp 2) ≈ total mass of organics (LOP + VOP) obtained without catalyst.

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Results

Elemental composition of organic phases.

%	Exp 1		Exp 2
	Viscous	Light	Organic
C	70.54	85.92	79.55
H	8.76	11.83	9.85
N	9.99	1.80	8.27
S	1.02	0.18	0.83
O[c]	9.69	0.27	1.5

[c] oxygen calculated by difference

Using γ-Al_2O_3:

✓great reduction of O content
✓C and H contents very similar to conventional fuels (*)
x N and S contents greater than conventional fuels (*)

(*) Bahadur, N., Boocok, D., Konar,S., Energy Fuels 9 (1995) 248-256

Results

Organic phase properties:

O/C ratio, H/C ratio and HHV values

	Material	O/C	H/C	HHV (MJ/kg)
Exp 1	Light organic phase	0.002	1.65	41.6
	Viscous organic phase	0.10	1.49	31.4
Exp 2	Organic phase	0.01	1.48	41.3
Exp 3	Organic phase	n.a	n.a	40.3

*n.a. not analized

HHV of the organic phase (exp. 2, 3) → possible use as a fuel (40-45 MJ/kg)

The catalyst load had more influence in the organic phase yield than in its HHV.

Results

Organic phase properties:

Kinematic viscosity, dinamic viscosity and density values at 32 ºC

	Material	Kinematic viscosity (cSt)	Dinamic viscosity (mPa*s)	Density (kg/dm^3)	API gravity
Exp 1	Viscous organic phase	140	122	0.87	<10
Exp 2	Organic phase	21	19	0.91	13
Exp 3	Organic phase	24	22.	0.92	21

Viscosity of the organic phase enhanced with the catalytic process → promising values for its use as a fuel

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Conclusions

- The enhancement of the fuel properties of pyrolysis liquids from sewage sludge by means of a catalytic treatment with γ-Al_2O_3 of the pyrolysis vapours generated has been studied in a fixed bed.

- Using γ-Al_2O_3 as a catalyst a more homogeneous pyrolysis liquid could be obtained. With a load of 94 g of catalyst the yield to the organic phase did not decrease significantly respect to a pyrolysis experiment without catalyst.

- Using activated γ-Al_2O_3 long carboxylic acids were converted into products with very little or no oxygen, like aliphatic and aromatic hydrocarbons.

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Conclusions

- The organic phase obtained in the catalytic process with activated γ-Al_2O_3 had a greater HHV in comparison to the viscous organic phase.

- The H/C ratio of the organic phase was very similar to that of a conventional fuel.

- The organic phases obtained in the catalytic process had significantly minor viscosity values than those of the viscous organic phase.

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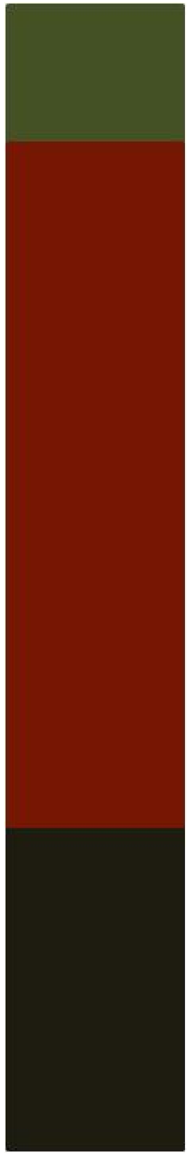
LIQUID: Due to the different properties of these 3 phases, they can not be mixed and used jointly.

Picture of the liquid after centrifugation.



Light organic phase: (Yield = 2.3 wt%)

•Composition: aliphatic hydrocarbons, steroids and triglycerides (no water).

•Physicochemical properties: HHV ~ 43 MJ/kg, ρ = 0.94 kg/dm^3, μ ~ 22 cP, pH = 8, moderate nitrogen (2.4 wt%) and sulfur (0.2 wt%) contents.

Aqueous phase: (Yield = 20.7 wt%)

•Composition: water (around 70 wt%), aminosugars, acids (C3-C9), phenolic compounds, nitrogen-containing compounds and levoglucosan.

•Physicochemical properties: HHV < 15 MJ/kg and high nitrogen content (7.0 wt%).

Heavy organic phase: (Yield = 9.8 wt%)

•Composition: triglycerides, aminosugars, phenolic compounds, nitrogen-containing compounds, fatty alcohols, fatty acids and a moderate water content (~7 wt%).

•Physicochemical properties: HHV ~ 31 MJ/kg, pH = 8-9, μ ~ 430 cP @20 ºC, high nitrogen (8.8 wt%) and sulfur (1.0 wt%) contents, no soluble in diesel and bio-diesel.

Methods

Operational conditions

- A new fixed bed reactor was set up in addition with the fluidized bed plant. Table III shows the most important operational conditions selected to carry out the sewage sludge pyrolysis experiments.
- Feed rate of 6 g/min of sewage sludge and a nitrogen flow of 4.4 dm^3 (NTP)/min was kept in each experiment (Fonts et Al, Azuara et Al).
- Since physical characteristics of sewage sludge enabled good fluidization behaviour, no fluidization agents, such as sand, were added to the bed.