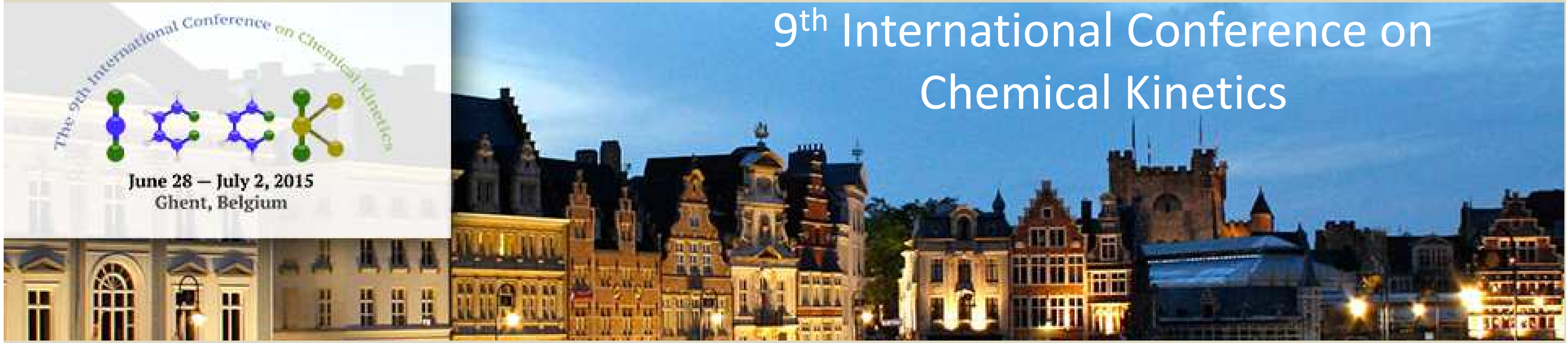

LIQUID KINETIC STUDY OF THE CATALYTIC CRACKING OF WASTE MOTOR OIL FOR OBTAINING DIESEL LIKE FUELS IN A BATCH PROCESS

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USFQ LaDEA Laboratorio de Desarrollo de Energías Alternativas

Outline

- Background information
- Motivation
- Characterization of waste motor oil
- Previous investigations
- Experimental results
- Conclusions
- Further investigations

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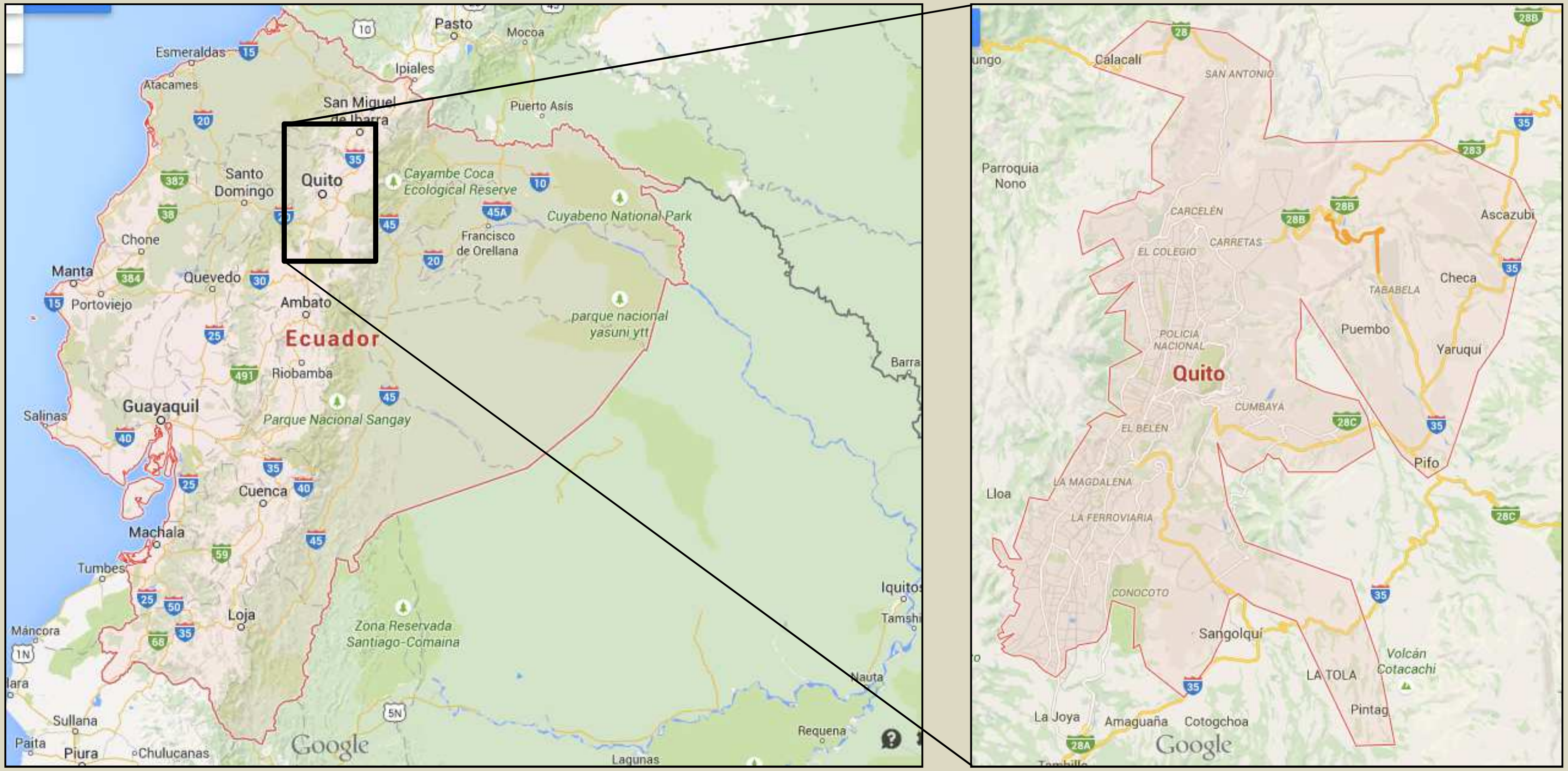
Background information



Background information

Quito – Ecuador

Altitude 2850 m (9350 ft) above sea level

Universidad San Francisco de Quito

http://at3w.com/upload/imagenes/san_francisco_university.jpg

Background information

Universidad San Francisco de Quito

Background information

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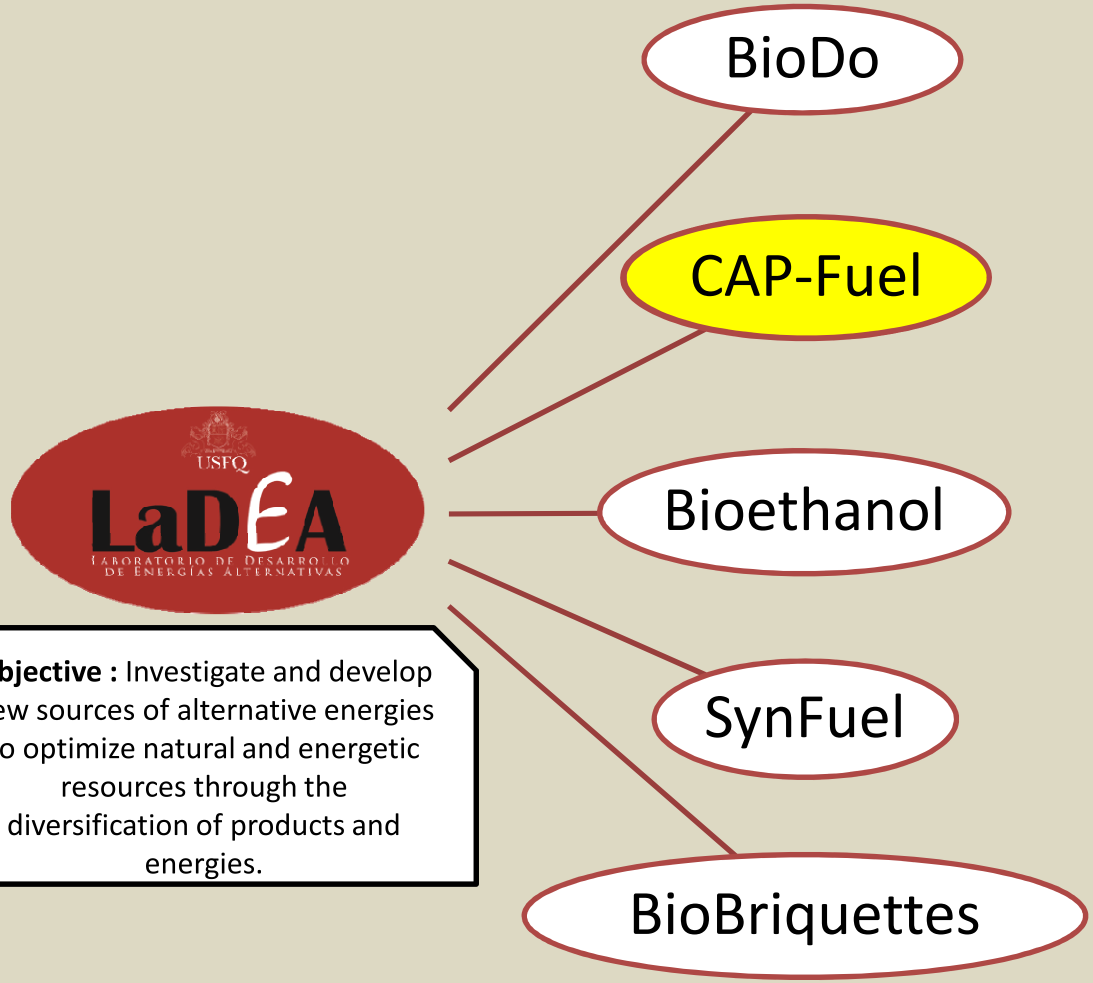
Background information



Objective : Investigate and develop new sources of alternative energies to optimize natural and energetic resources through the diversification of products and energies.

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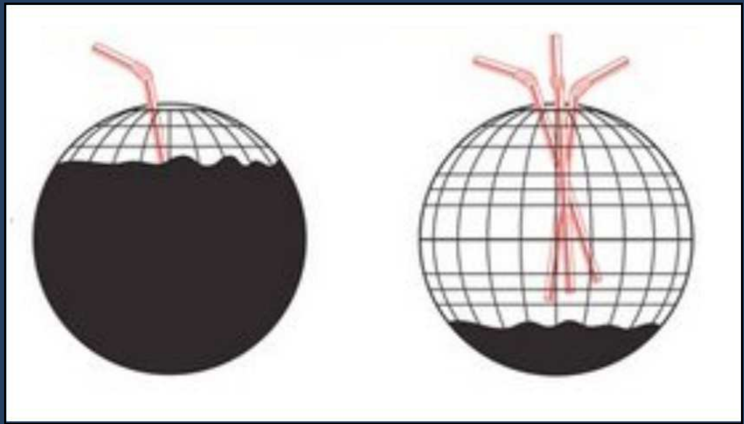
Motivation

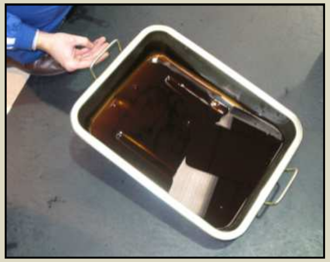


Depleting oil reserves

Unstable fuel prices

Environmental Awareness

Motivation



Motor oil → Change oil → Waste motor oil

Waste motor oil storage

Raw material

Motivation

http://www.easyvectors.com/assets/images/vectors/afbig/aa0313e70f670e8f8bc9d830c4722f42-earth-clip-art.jpg

http://www.fordesigner.com/pic/zip01/b_1301627171111.jpg

Produce

https://www.colourbox.com/preview/5980087-toxic-hazardous-waste-barrels-icon.jpg

1.2 billion cars
(Shiung, 2011)

24 million tons / year
(Tencer, 2011)

1 gallon used motor oil

Contaminate

1 million gallons of water
(EPA, 2014)

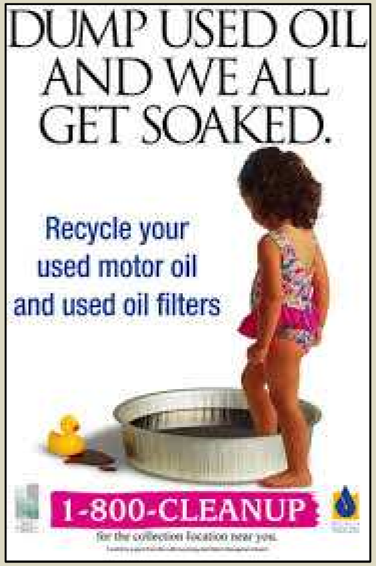
Motivation

Waste motor oil is a ***hazardous*** contaminant

- Lead
- Cadmium
- Arsenic
- Dioxins
- Benzene
- Polycyclic aromatics

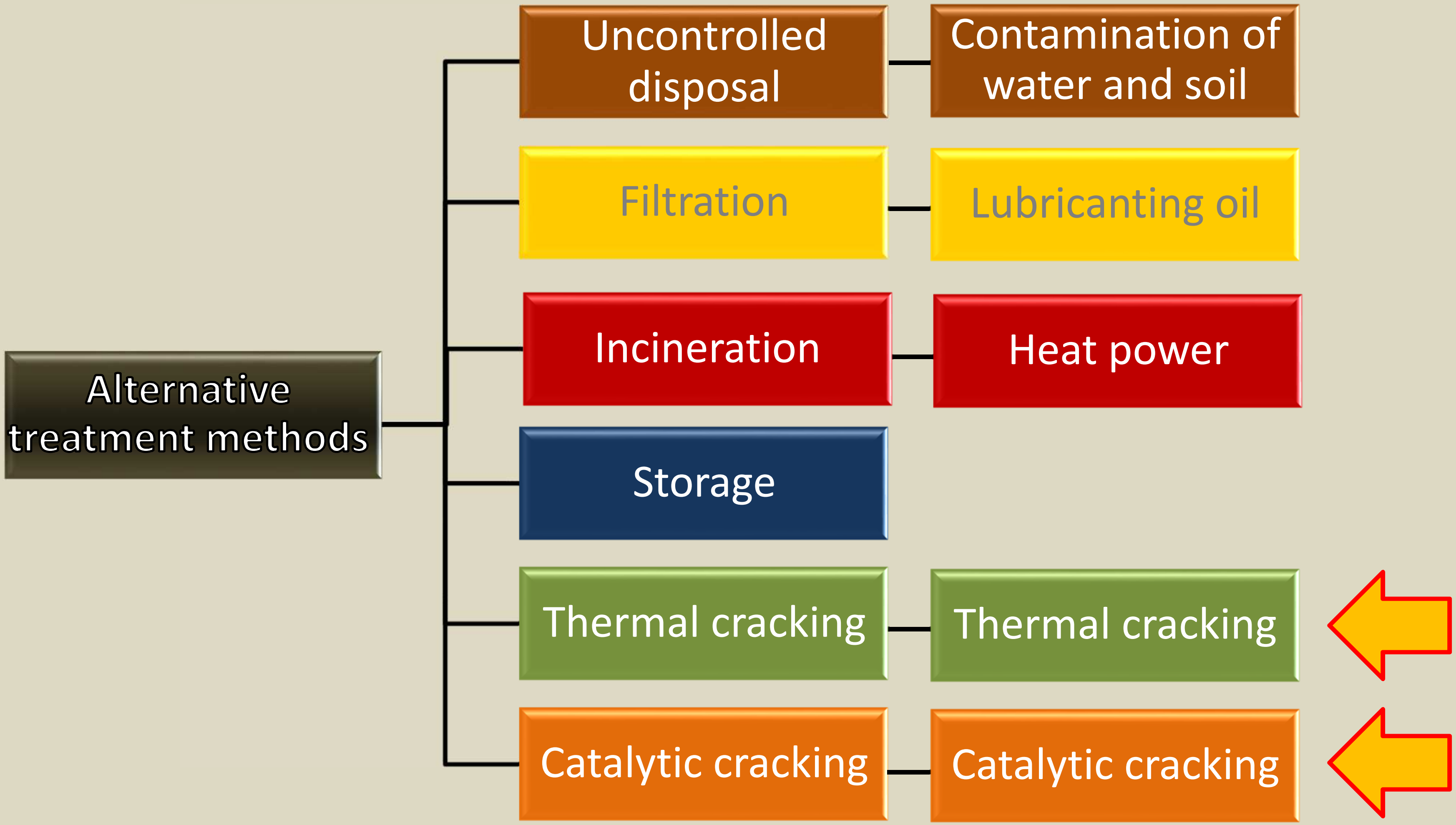
Its inappropriate disposal can harm humans, plants, animals, fish and shellfish.

http://www.sfenvironment.org/sites/default/files/editor-uploads/toxics/oil_and_filters.jpg



https://encrypted-tbn0.gstatic.com/images?q=tbn:ANd9GcRZvyd0qT7wRF-PGJwm_7NVFqkpTNQ3RlCf_2znDlg42llbTbvrPA

Motivation


Alternative treatment methods
Uncontrolled disposal
Contamination of water and soil
Filtration
Lubricanting oil
Incineration
Heat power
Storage
Thermal cracking
Thermal cracking
Catalytic cracking
Catalytic cracking

Outline

- Background information
- Motivation
- **Characterization of waste motor oil**
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Characterization of waste motor oil

Characterization methods - **American Society for Testing and Materials (ASTM)**

Analysis performed at Laboratory for Quality Control of Clean Products Terminal "El Beaterio"

Table 1 Characterization methods

Norm	Method
ASTM D56	Standard Test Method for Flash Point by Tag Closed Cup Tester
ASTM D86	Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure
ASTM D1298	Standard Test Method for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method
ASTM D2270	Standard Practice for Calculating Viscosity Index from Kinematic Viscosity at 40 and 100ºC
ASTM D4294	Standard Test Method for Sulfur in Petroleum and Petroleum Products by Energy-Dispersive X-Ray Fluorescence

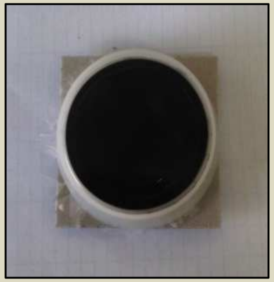
Characterization of waste motor oil

Characterization methods - **American Society for Testing and Materials (ASTM)**

Table 2 Characterization of waste motor oil

	Flash Point [°C]	Distillation [°C]	API gravity [°API]	Kinematic Viscosity [cSt]	Sulfur content [%p/p]
Diesel #2	Min 51	Max 360	32-39	2.5-6	Max 0.7
Waste motor oil	69	380	29.6	113.14	0.364

Waste motor oil and cracking products



Determination of sulfur content

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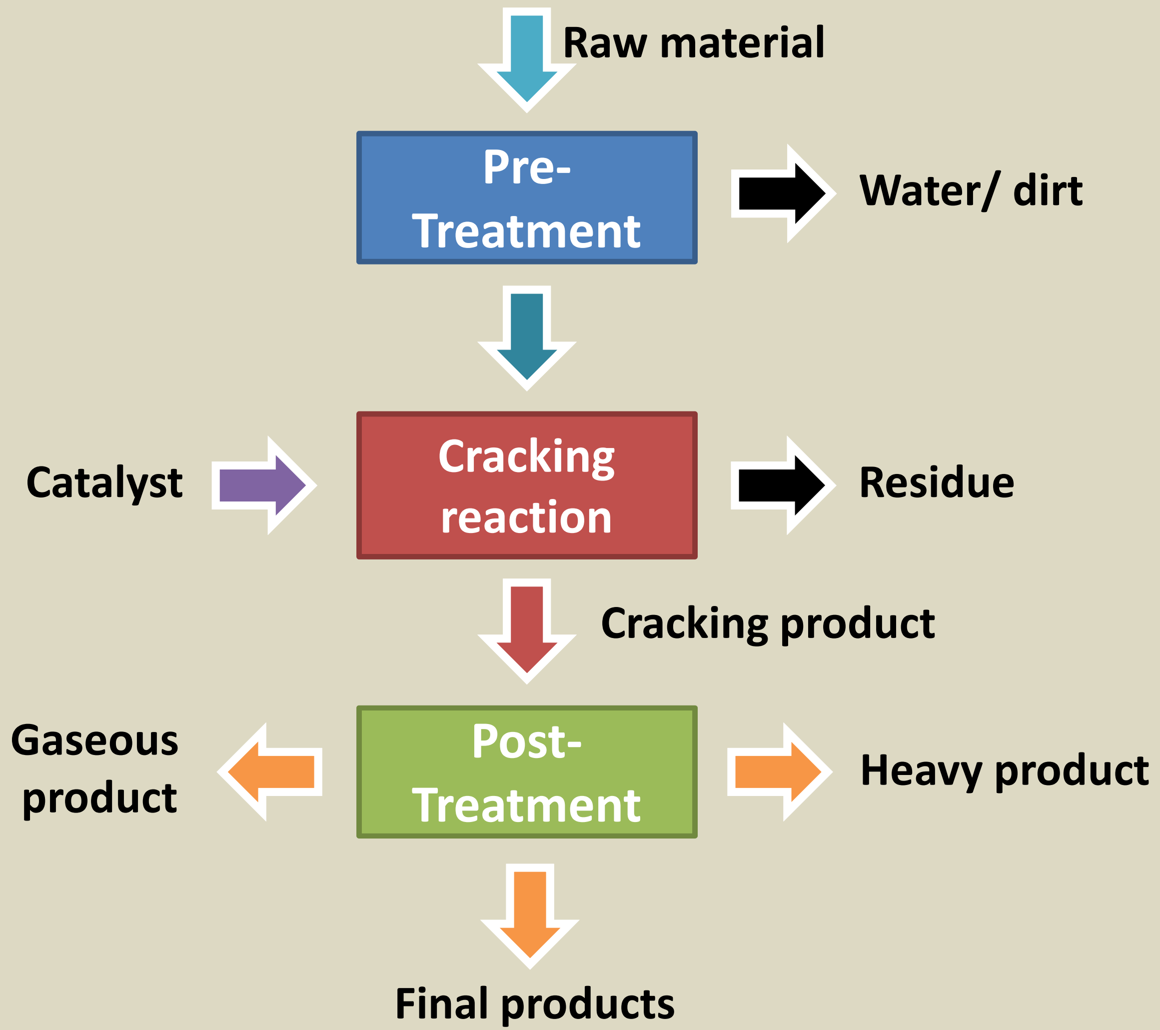
Previous investigations

- **Process Diagram**



Previous investigations

- **Materials**
  - Glass batch reactor
  - Cracking equipment

- **Constant parameters**
  - 100 g of waste motor oil
  - 1g of catalyst

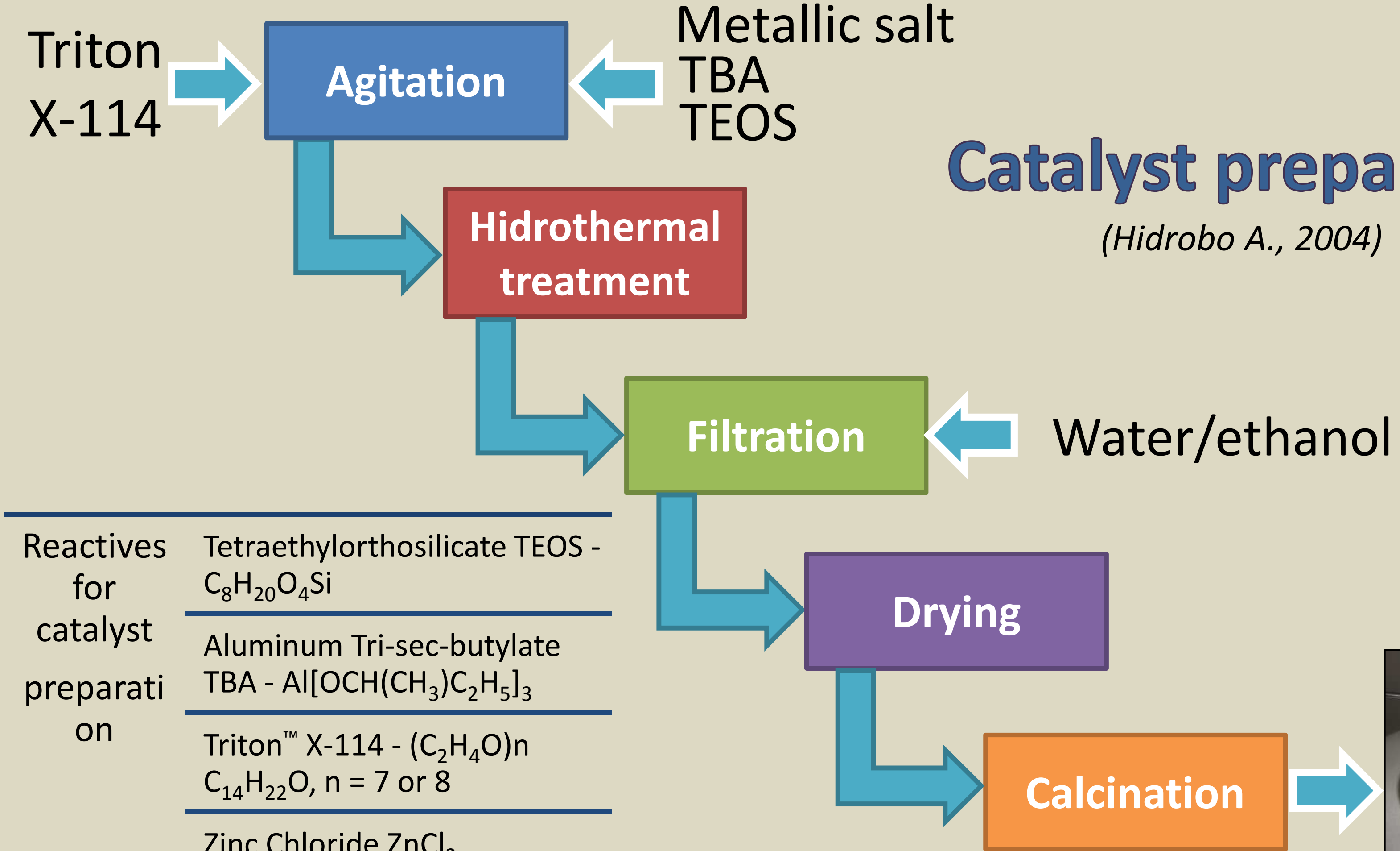
- **Variables**

Temperature [C°]	300	310	320	330
Catalyst	--	Al/Si	Al/Si-Zn 1%	Al/Si-Zn 2%

Previous investigations

Catalyst preparation

(Hidrobo A., 2004)



Catalyst

Reactives for catalyst preparation	Tetraethylorthosilicate TEOS - $C_8H_{20}O_4Si$
	Aluminum Tri-sec-butylate TBA - $Al[OCH(CH_3)C_2H_5]_3$
	Triton™ X-114 - $(C_2H_4O)n$ $C_{14}H_{22}O$, n = 7 or 8
	Zinc Chloride $ZnCl_2$

Previous investigations

Catalyst for cracking reaction

- Carioca — 350°C
- Grace Davison — 355°
- Al/Si (Cu, Ni, Zn) — 300-330 °C

FÁBRICA CARIOCA DE CATALISADORES

http://www.fccsa.com.br/templates/fccsa2010/?y=1&cod_idioma=3

GRACE Davison

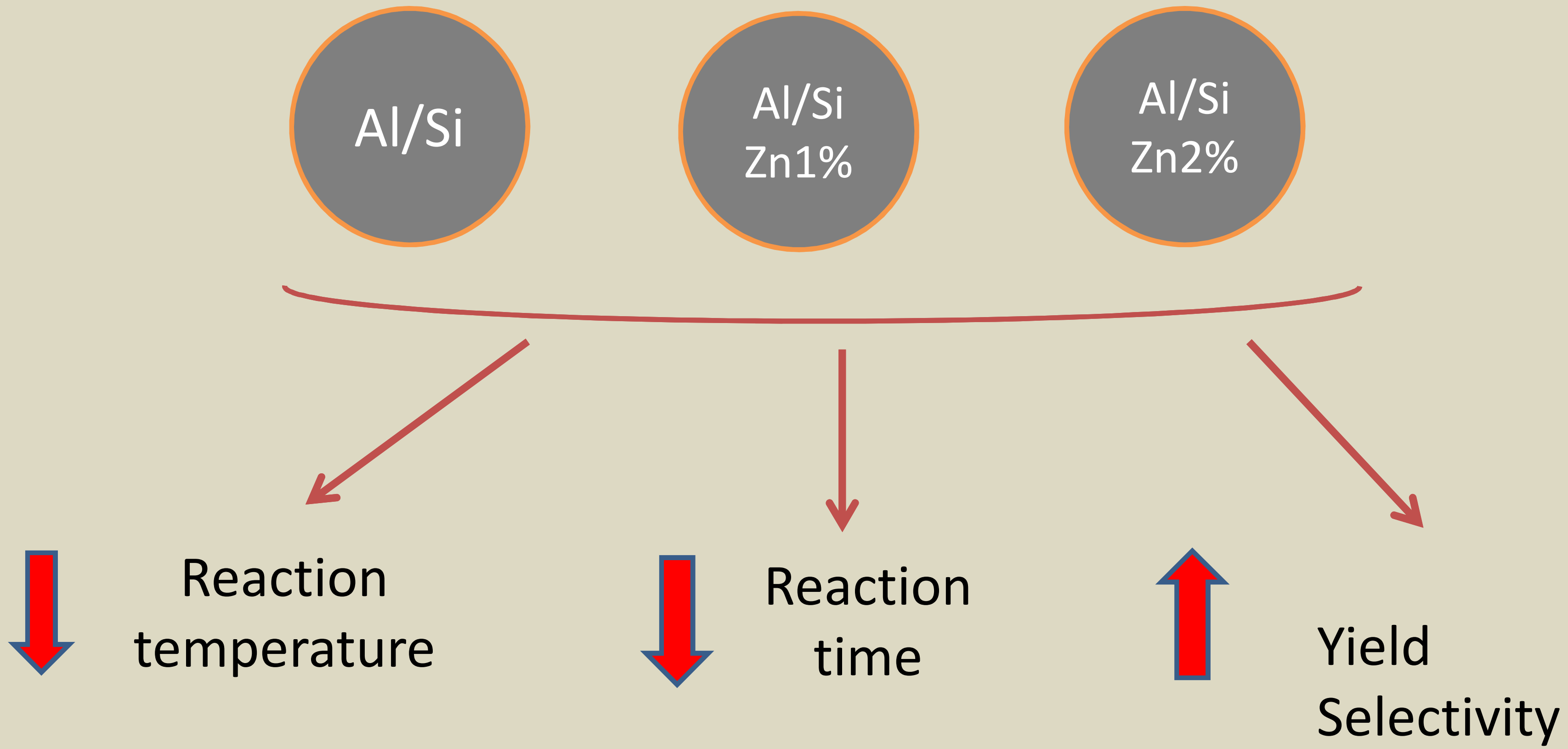
http://img.over-blog.com/300x63/4/10/89/98/logo_GraceDavison.gif

Previous investigations

Table 3 Previous studies on cracking reaction (Benedik S. and Almeida D., in progress)

Abreviation	Impregnated metal	Cracking Temperature [°C]	Yield [%]
Blank	-	356	57
Carioca	-	354	60
Grace Davison	-	355	61
Al/Si	-	339	62
Al/Si-Cu1%	Copper	353	62
Al/Si-Zn 1%	Zinc	333	63
Al/Si-Zn 2%	Zinc	285	65
Al/Si-Ni1%pH	Nickel	325	62

Previous investigations



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Experimental Results

Cracking reaction

$$A_{(l)} \rightarrow 2B_{(l)} + C_{(g)}$$

$$C_{30}H_{62} \rightarrow C_{13}H_{28} + C_{12}H_{24} + C_{5}H_{10}$$

Waste motor oil in a glass batch reactor

+

Catalyst

Cracking reaction →

Cracking product

Experimental Results

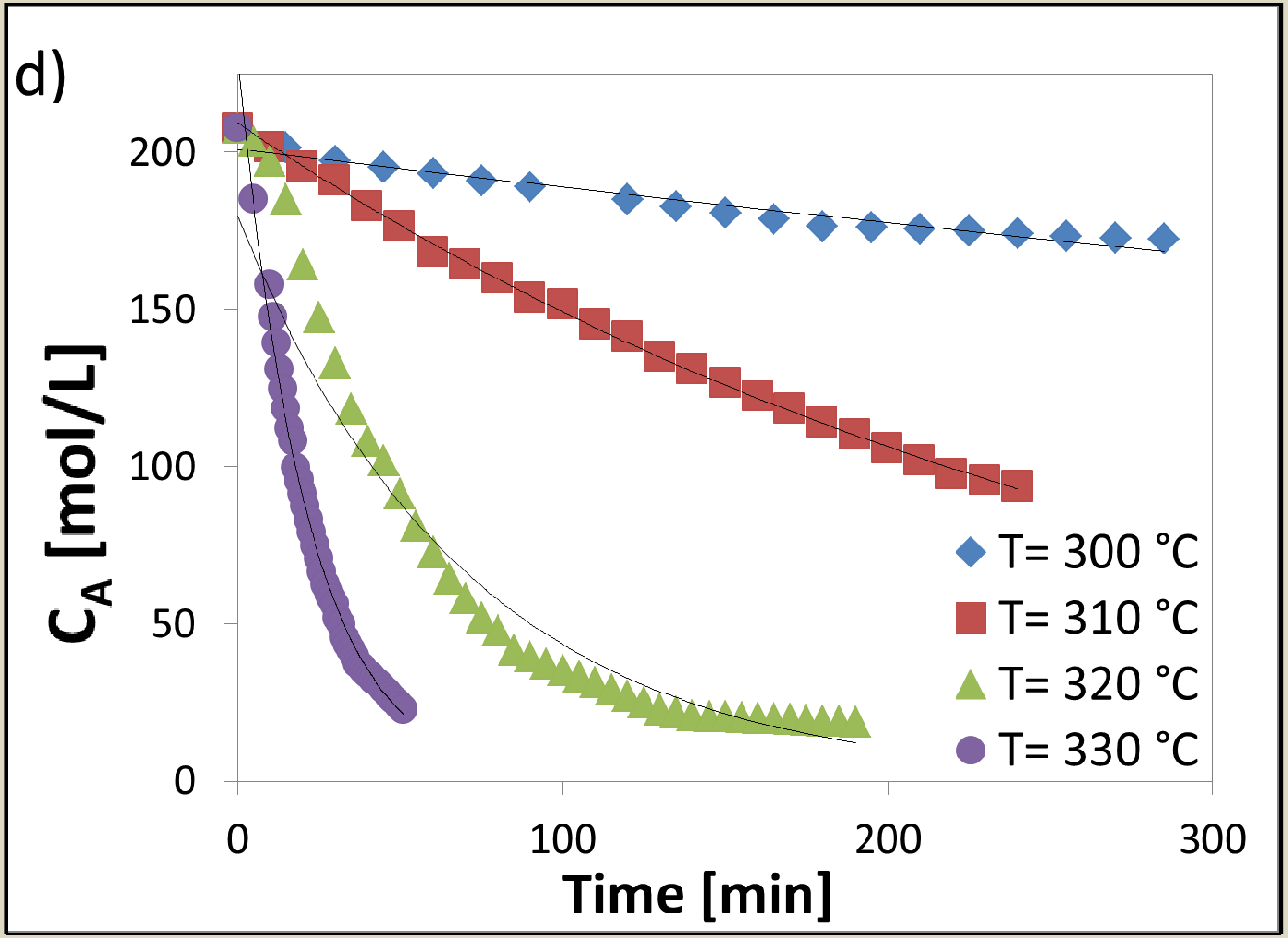

Figure 1 Concentration of waste motor oil during cracking reaction

a) Thermal cracking reaction.

b) Catalytic cracking reaction Al/S matrix.

c) Catalytic cracking reaction Al/Si matrix doped with Zinc 1%.

d) Catalytic cracking reaction Al/Si matrix doped with Zinc 2%.

Experimental Results

Table 4 Summarized results of exponential regression

Experiment	Temperature [°C]	Differential analysis		
		a	b	R^2
Thermal	300	21165	-0.002	0.9814
	310	200.7	-0.002	0.9751
	320	199.59	-0.002	0.9913
	330	224.5	-0.026	0.9677
Al/Si	300	204.02	-0.001	0.8951
	310	207.51	-0.001	0.9935
	320	202.66	-0.003	0.947
	330	201.29	-0.033	0.9828
Al/Si Zn 1%	300	200.7	-0.0005	0.904
	310	199.78	-0.004	0.9865
	320	188.31	-0.008	0.9837
	330	237.88	-0.033	0.9914
Al/Si Zn 2%	300	201	-0.0006	0.9452
	310	209.36	-0.003	0.9989
	320	179.54	-0.014	0.9449
	330	230.27	-0.047	0.9936

Experimental Results

- Potencial law model

$$C_{30}H_{62} \rightarrow C_{13}H_{28} + C_{12}H_{24} + C_{5}H_{10}$$

$$A_{(l)} \rightarrow 2B_{(l)} + C_{(g)}$$

$$R_A = [k(T)]\,[fn\,(C_A)]$$

$$R_A = \frac{dC_A}{dt} = -k\,C_A^n$$

$$\log_{10}\left(-\frac{dC_A}{dt}\right) = \log_{10} k + n\,\log_{10} C_A$$

Experimental Results

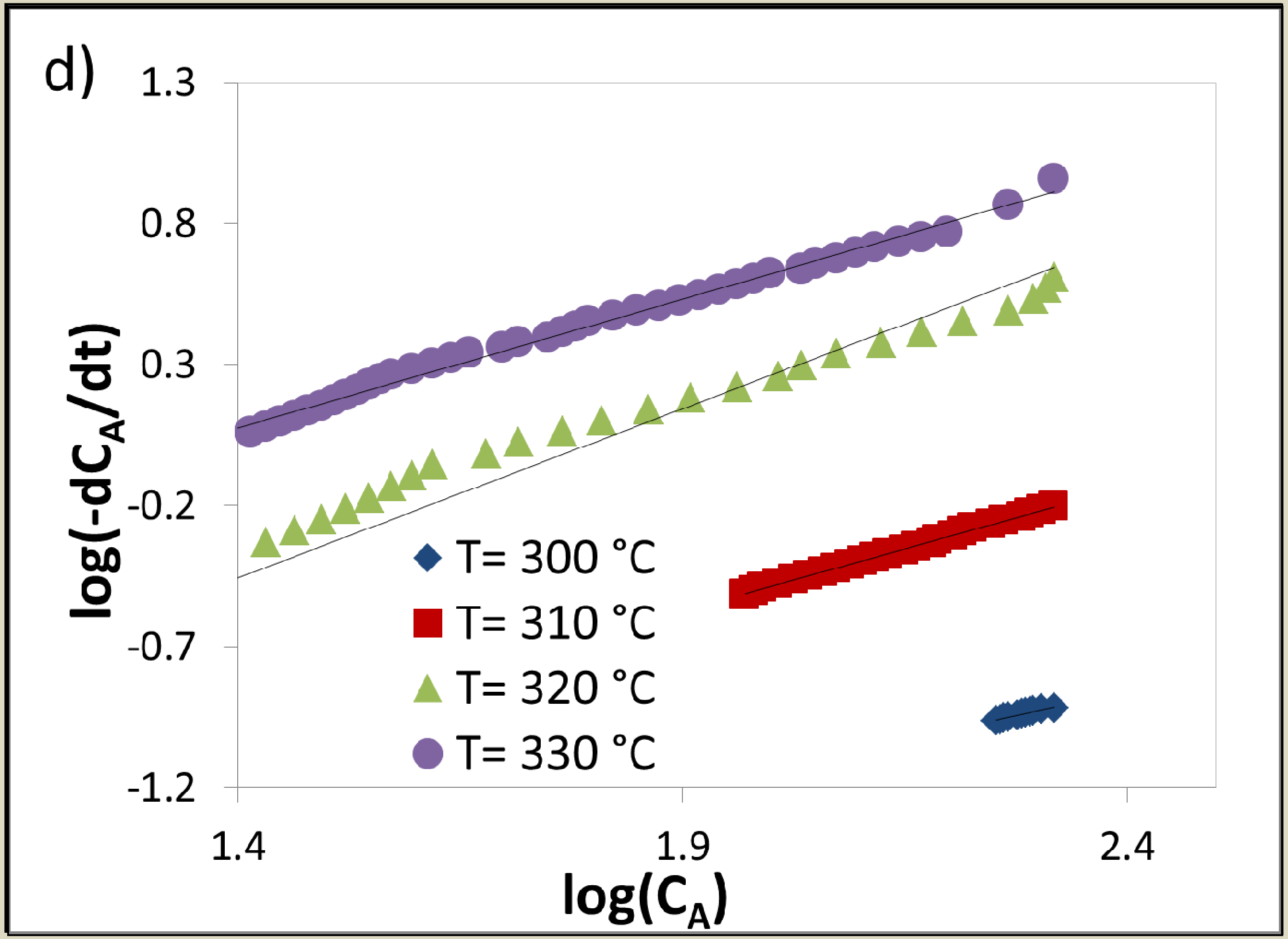

Figure 2 Linear regression for experimental data

a) *Thermal cracking reaction.*

b) *Catalytic cracking reaction Al/S matrix.*

c) *Catalytic cracking reaction Al/Si matrix doped with Zinc 1%.*

d) Catalytic cracking reaction Al/Si matrix doped with Zinc 2%.

Experimental Results

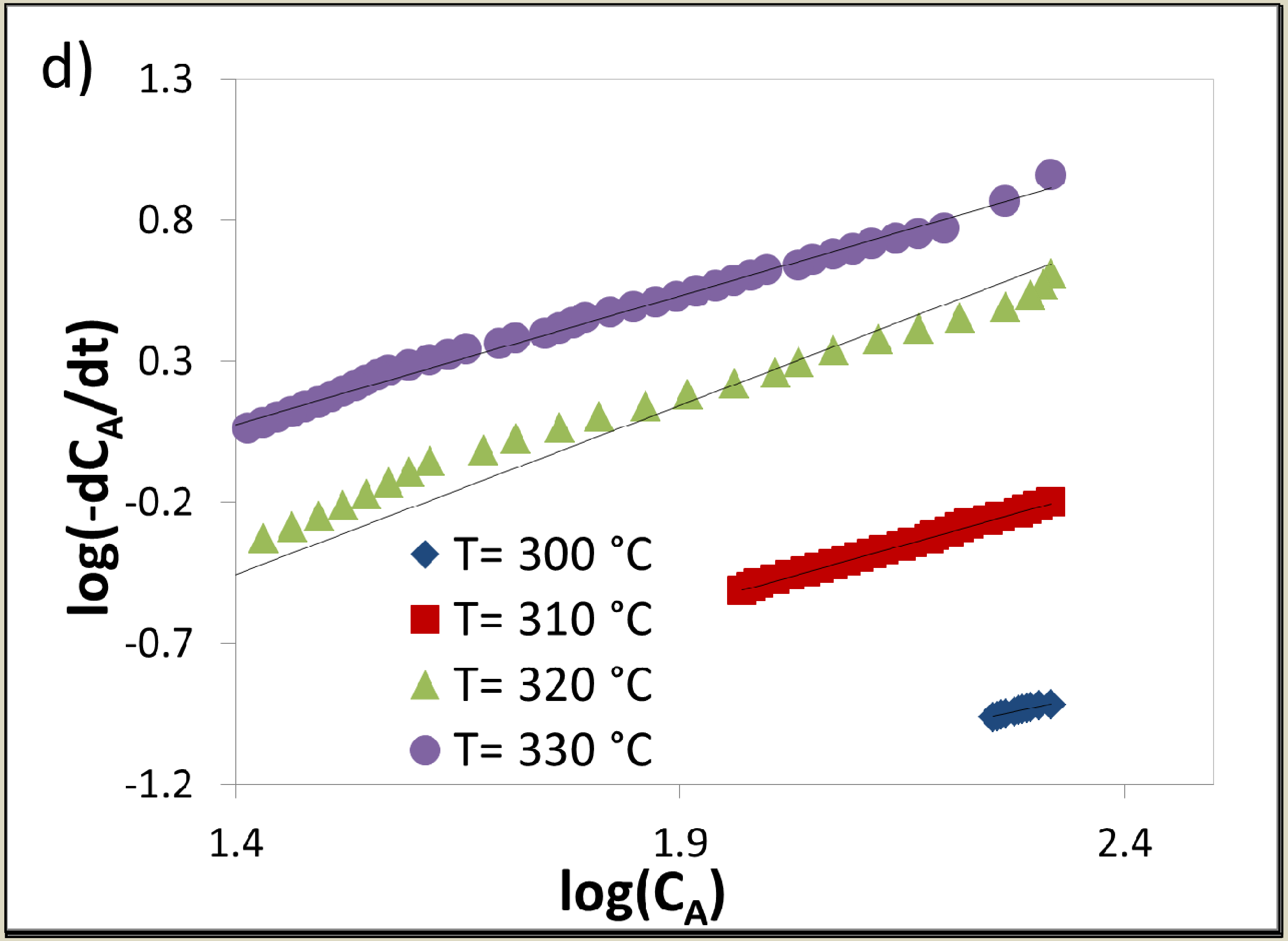

Figure 2 Linear regression for experimental data

a) Thermal cracking reaction.

b) Catalytic cracking reaction Al/S matrix.

c) Catalytic cracking reaction Al/Si matrix doped with Zinc 1%.

d) Catalytic cracking reaction Al/Si matrix doped with Zinc 2%.

Experimental Results

Table 5 Summarized results of exponential regression

Experiment	Temperature [°C]	Temperature dependence		
		m	b	R^2
Thermal	300	1.0038	-2.7098	0.9751
	310	1.2310	-3.2380	0.9814
	320	0.8022	-2.2447	0.9913
	330	0.9859	-1.5738	0.9677
Al/Si	300	0.8876	-2.7453	0.8951
	310	0.8188	-2.5823	0.9935
	320	0.7154	-2.3449	0.9962
	330	0.9906	-1.4698	0.9828
Al/Si Zn 1%	300	0.7333	2.6937	0.9821
	310	0.8405	-2.1516	0.9819
	320	0.9946	-2.0923	0.9837
	330	0.9876	-1.4325	0.9914
Al/Si Zn 2%	300	0.7077	2.5536	0.9773
	310	0.8848	-2.2557	0.9989
	320	1.1992	-2.1346	0.9449
	330	0.9139	-1.2060	0.9936

Experimental Results

Table 6 Kinetic parameters of cracking reactions

Experiment	Temperature [°C]	Kinetic parameters		
		Reaction order, n[-]	Activation Energy, Ea [kJ/mol]	Reduction of Ea [%]
Thermal	300 310 320 330	1.0 ± 0.1	370.39	-
Al/Si	300 310 320 330	1.0 ± 0.1	304.39	17.82
Al/Si Zn 1%	300 310 320 330	0.8 ± 0.1	280.71	24.21
Al/Si Zn 2%	300 310 320 330	0.9 ± 0.2	278.37	24.84

Experimental Results

Table 7 Characterization of waste motor oil and product from cracking process

	Flash Point [°C]	Distillation [°C]	API gravity [°API]	Kinematic Viscosity [cSt]	Sulfur content [%p/p]
Diesel #2	Min 51	Max 360	32-39	2.5-6	Max 0.7
Waste motor oil	69	380	29.6	113.14	0.364
Thermal cracking	65	354	37.4	4.65	0.1614
Catalytic cracking Al/Si	68	342	38.9	4.67	0.1403
Catalytic cracking Al/Si Zn 1%	69	343	38.5	4.78	0.1305
Catalytic cracking Al/Si Zn 2%	70	345	39.1	4.72	0.1264

Experimental Results

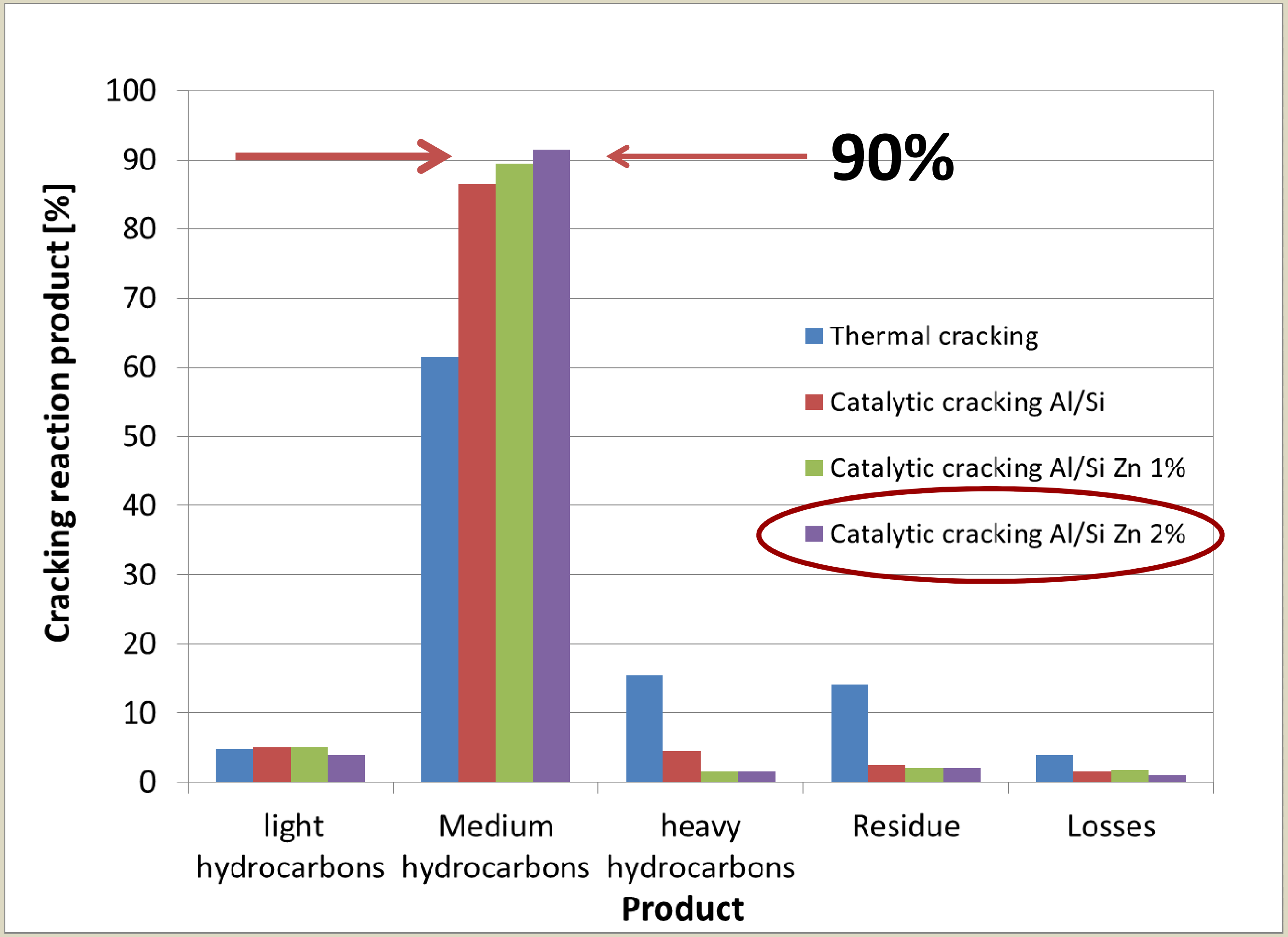

Figure 3 Products of cracking reactions

Experimental Results

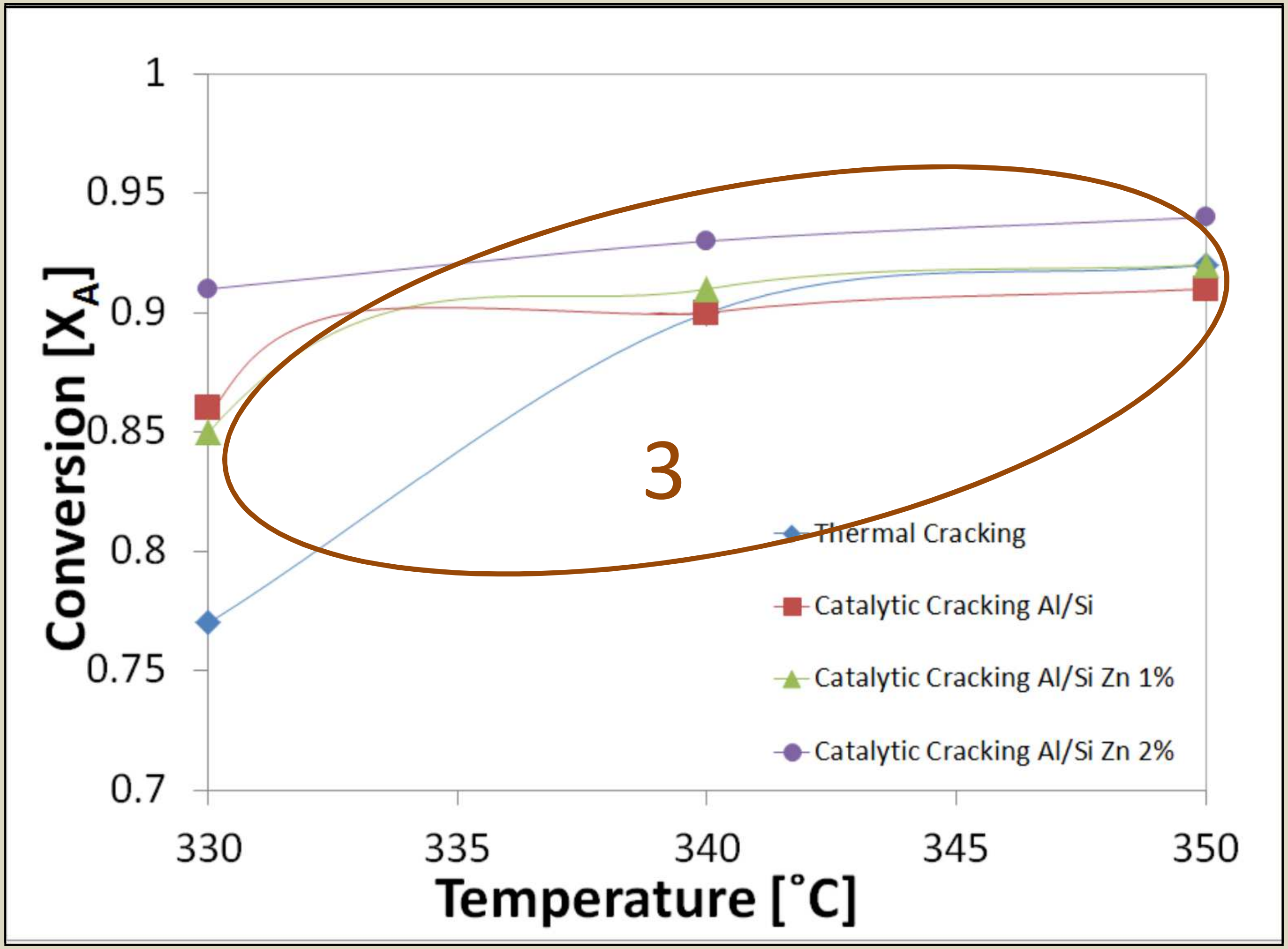

Figure 4 Conversion of the waste motor oil as function of temperature

Outline

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- Further investigations

Conclusions

Table 8 Summarized results

Parameter	Thermal cracking	Catalytic cracking Al/Si	Catalytic cracking Al/Si Zn 1%	Catalytic cracking Al/Si Zn 2%
Reaction order, n, [Ea]	1.0 ± 0.1	1.0 ± 0.1	1.0 ± 0.1	0.9 ± 0.2
Activation energy Ea [kJ/mol]	370.39	304.39	280.71	278.37
Reduction in activation energy [%]	-	17.82	24.21	24.84
Conversion X_A (T=330°C)	0.77	0.85	0.86	0.9

- The final product of the different processes of thermal and catalytic cracking meets all necessary requirements for diesel # 2.

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Design and construction of a fixed bed reactor for the conversion of waste motor oil into liquid fuels

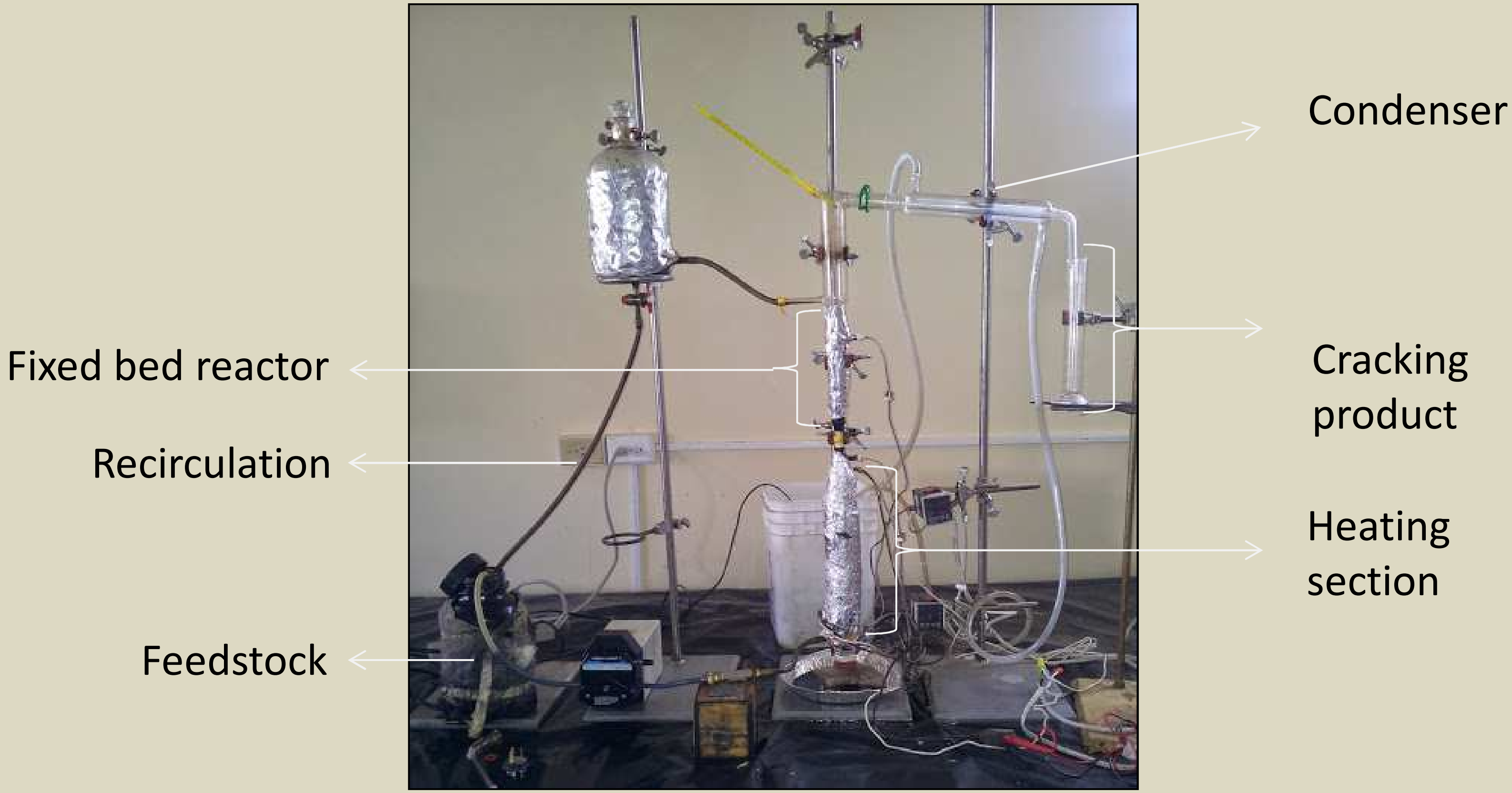

Figure 5 Glass fixed bed reactor

Further investigations

Design and construction of a fixed bed reactor for the conversion of waste motor oil into liquid fuels.

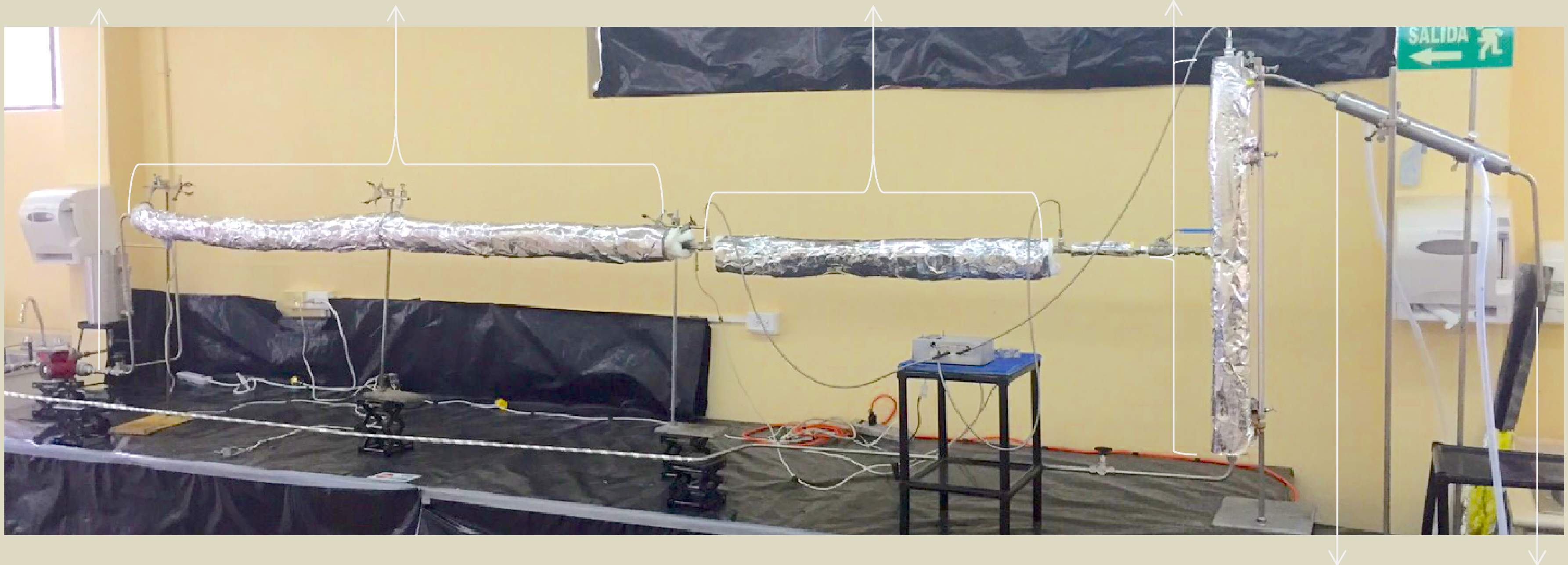

Figure 6 Stainless steel fixed bed reactor

Thank you for your attention!

Questions?

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