Catalytic Microwave-Assisted Biomass Pyrolysis for Distributed Biofuels and Chemicals Production

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UNIVERSITY OF MINNESOTA

OUTLINE

- Brief background and introduction – why microwave-assisted pyrolysis
- Mobile microwave-assisted pyrolysis system development
- Catalytic microwave assisted pyrolysis
- Non-thermal assisted catalytic reforming

Nature of Current Cellulosic Biomass Production

- Distributed production
- Transporting bulky biomass from scattering production sites to a central processing facility has been a key barrier to biomass utilization

Cellulosic Ethanol

- **40-50 million gallons/year cellulosic ethanol plants: cost over $300 million to build, need over 2,000 tons biomass per day.**
- **Furthermore, compared with corn ethanol production, additional processing costs are needed to convert cellulosic feedstock to fermentable sugars, which would raise feedstock-associated costs to as high as 70–80% of the final product cost, in additional to other technical and management challenges.**

Gasification and Fischer–Tropsch Liquid Biofuels

- **40-50 million gallons/year liquid fuel plants: cost about $1 billion to build, need over 3,000-4,000 tons biomass per day, and expensive to operate due to catalyst cost and safety issue related to high pressure and high temperature of the process, in additional other technical and management challenges.**

Large Scale Processes

- High capital investment
- High operation technicality
- High feedstock transportation and storage costs

Distributed Biomass Conversion Systems (DBCS)
-
A “Smaller” Solution

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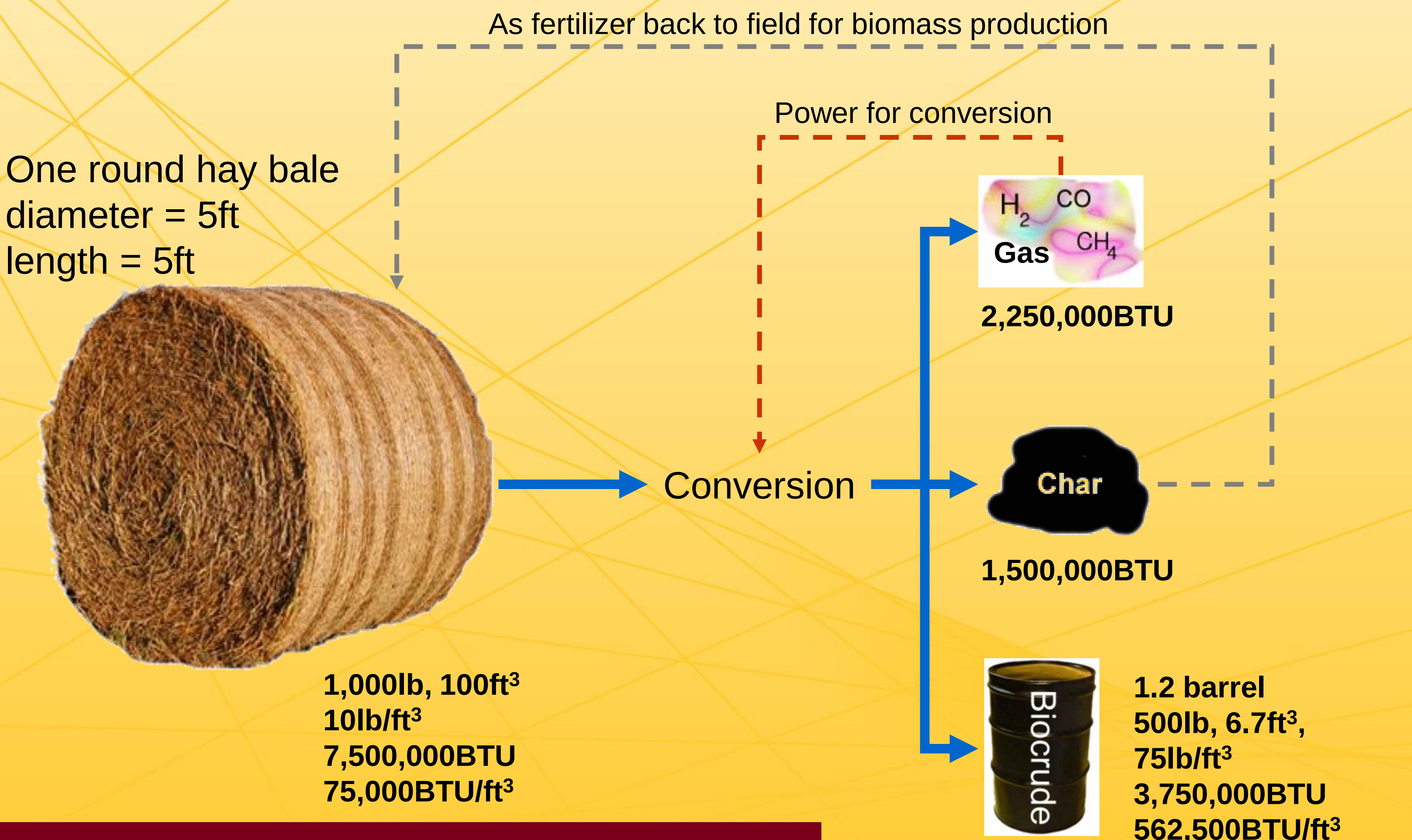
Bale to Barrel DBCS



Can be implemented on average size farms or small villages

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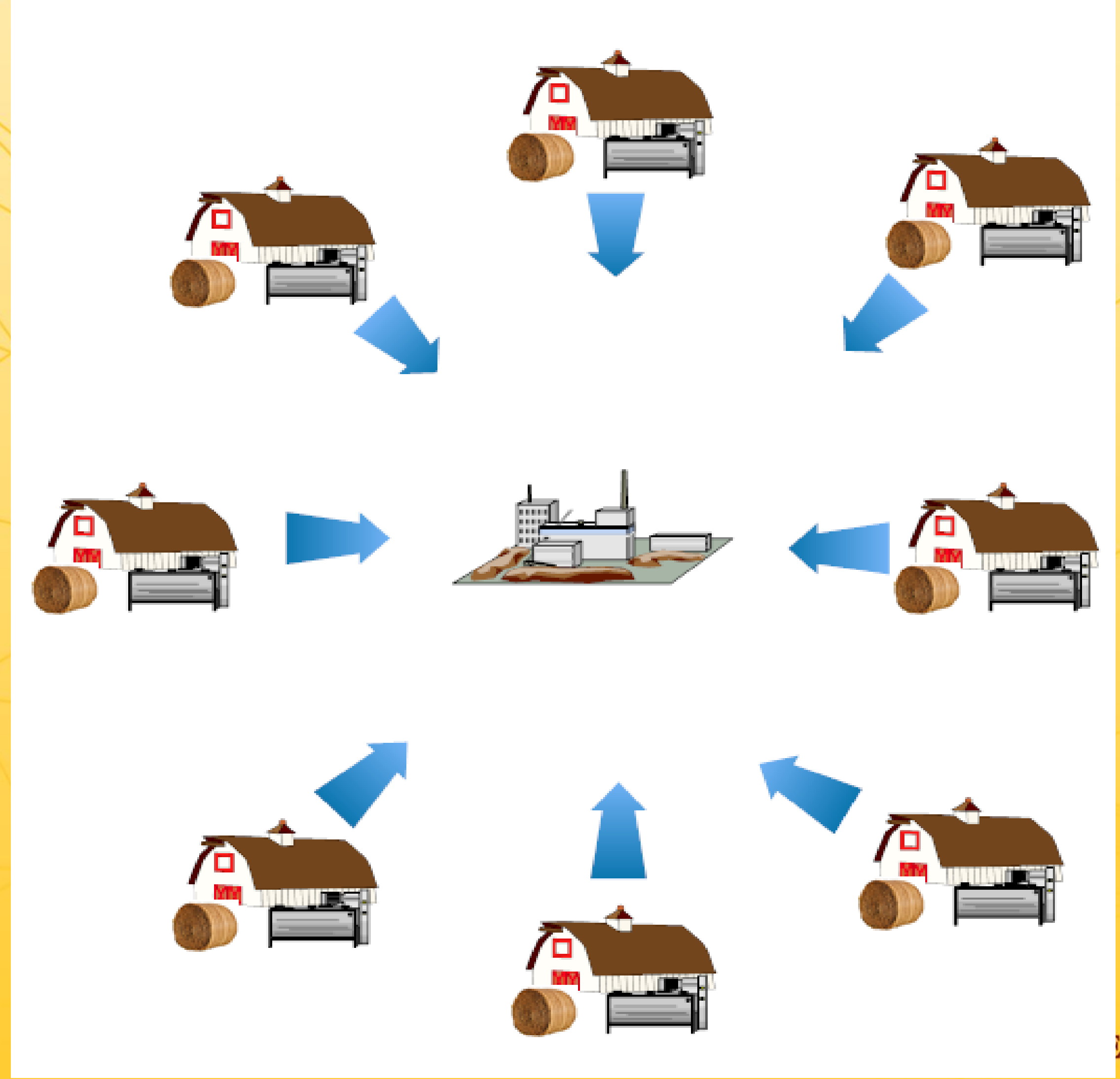
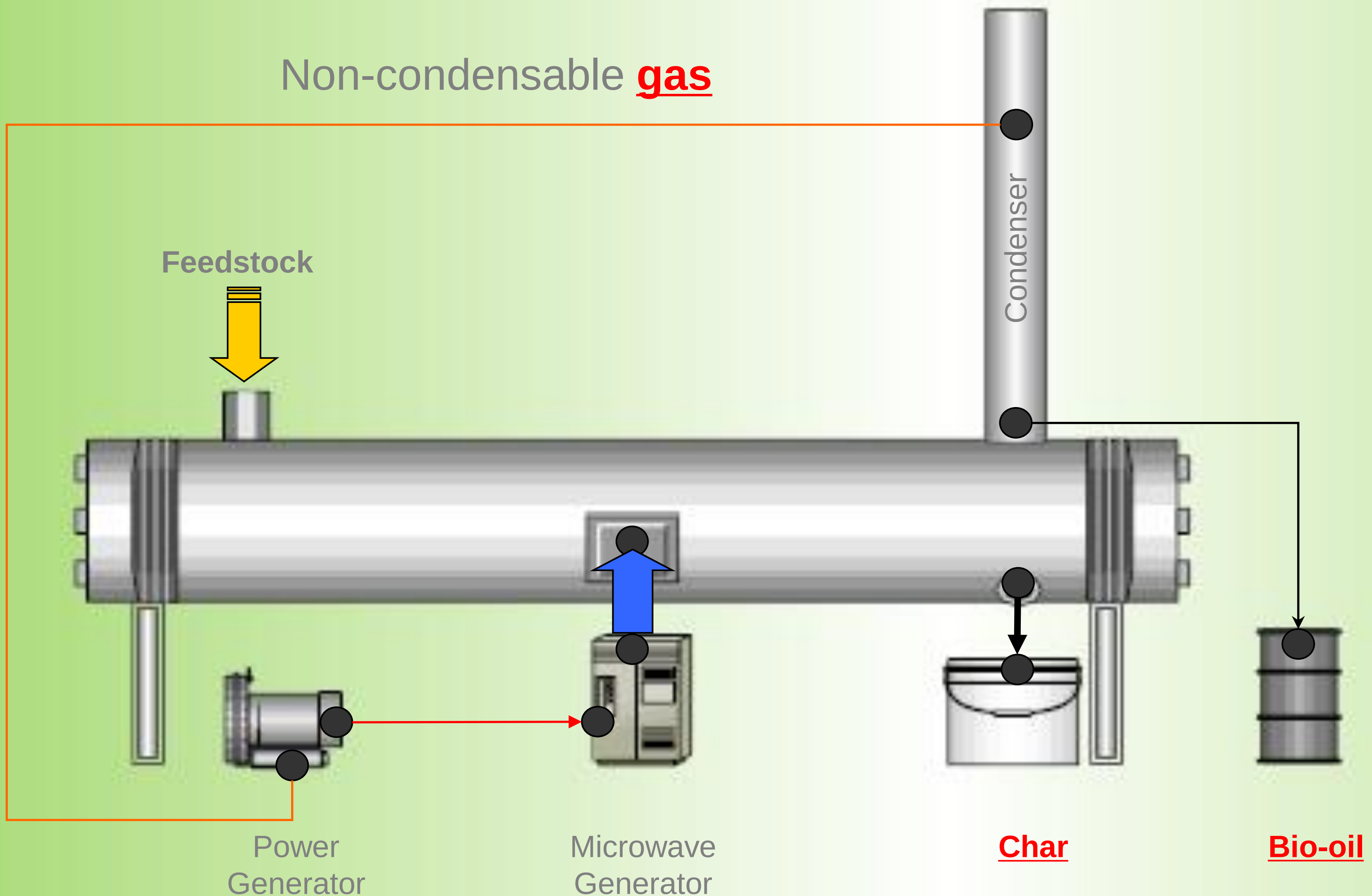
Distributed Biomass Processing Scheme



Microwave Assisted Pyrolysis (MAP) System



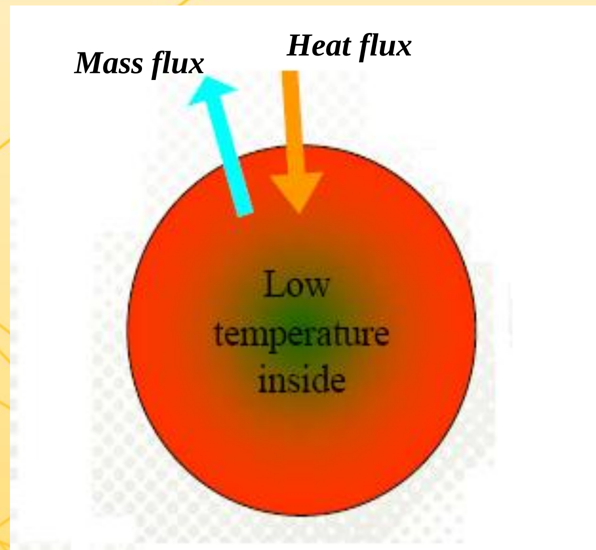
Microwave-Assisted Pyrolysis (MAP) System

Why MAP?

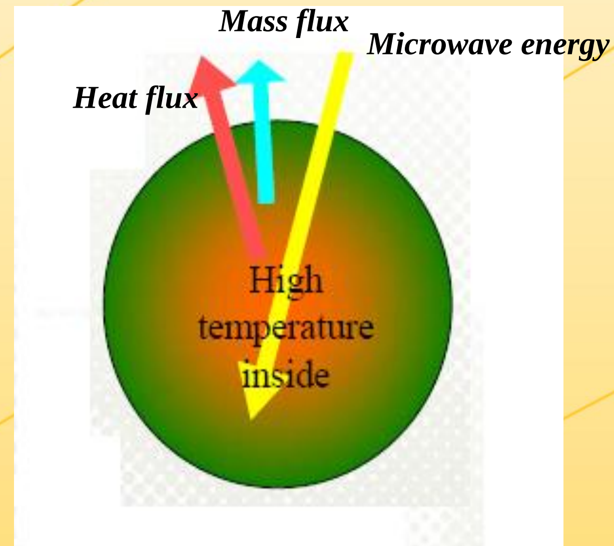
- Microwave heating is uniform and easy to control;
- It does not require high degree of feedstock grinding (e.g., large chunk of wood logs) and can handle mixed feedstock (e.g., municipal solid wastes);
- The conversion products (pyrolytic gas and bio-oils) are cleaner than those from gasification and conventional pyrolysis because our process does not have to use biomass powder and does not require agitation and fluidization;
- The syngas produced has higher heating value since it is not diluted by the carrying gas for fluidizing the biomass materials;
- Exothermic reactions (chemical reaction that releases energy and microwave plasma effect) can be maintained through careful control of the process parameters and therefore MAP is energy efficient; and
- Microwave heating is a mature technology and development of microwave heating system for biomass pyrolysis is of low cost.
- Scalable, portable, mobile – distributed conversion of biomass

Micorwave Pyrolysis of Aspen

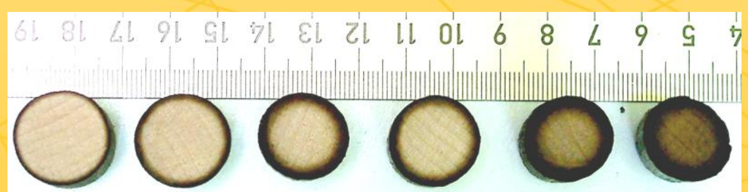
Canola Seed Press Cake



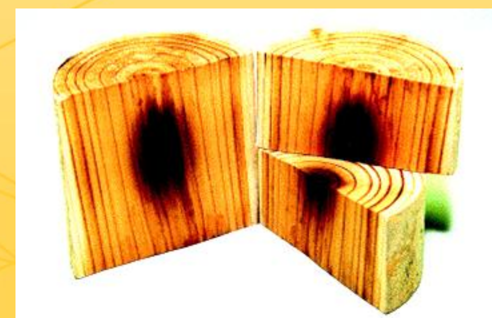
a. conventional heating approach



b. Microwave heating approach



c. Pyrolysis front development with conventional heating

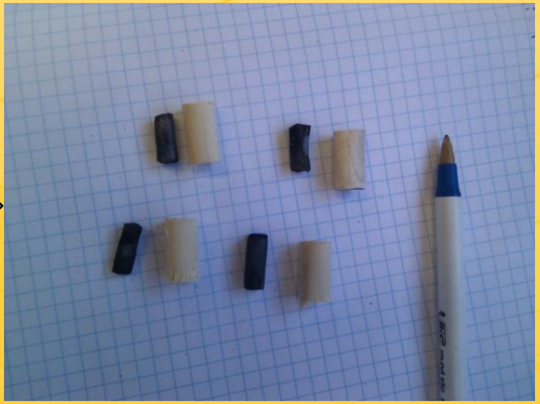


d. Pyrolysis front development with microwave heating

Particle size effect in MAP

Size (diameter, inch)	1/8	3/8	1/2	5/8	3/4
Oil yield (wt%)	55.15	60.40	60.52	55.06	54.25
Char yield (wt%)	18.96	16.94	18.91	15.36	17.11

Note:
Feedstock: Poplar Wood
Microwave Power: 1250 Watt

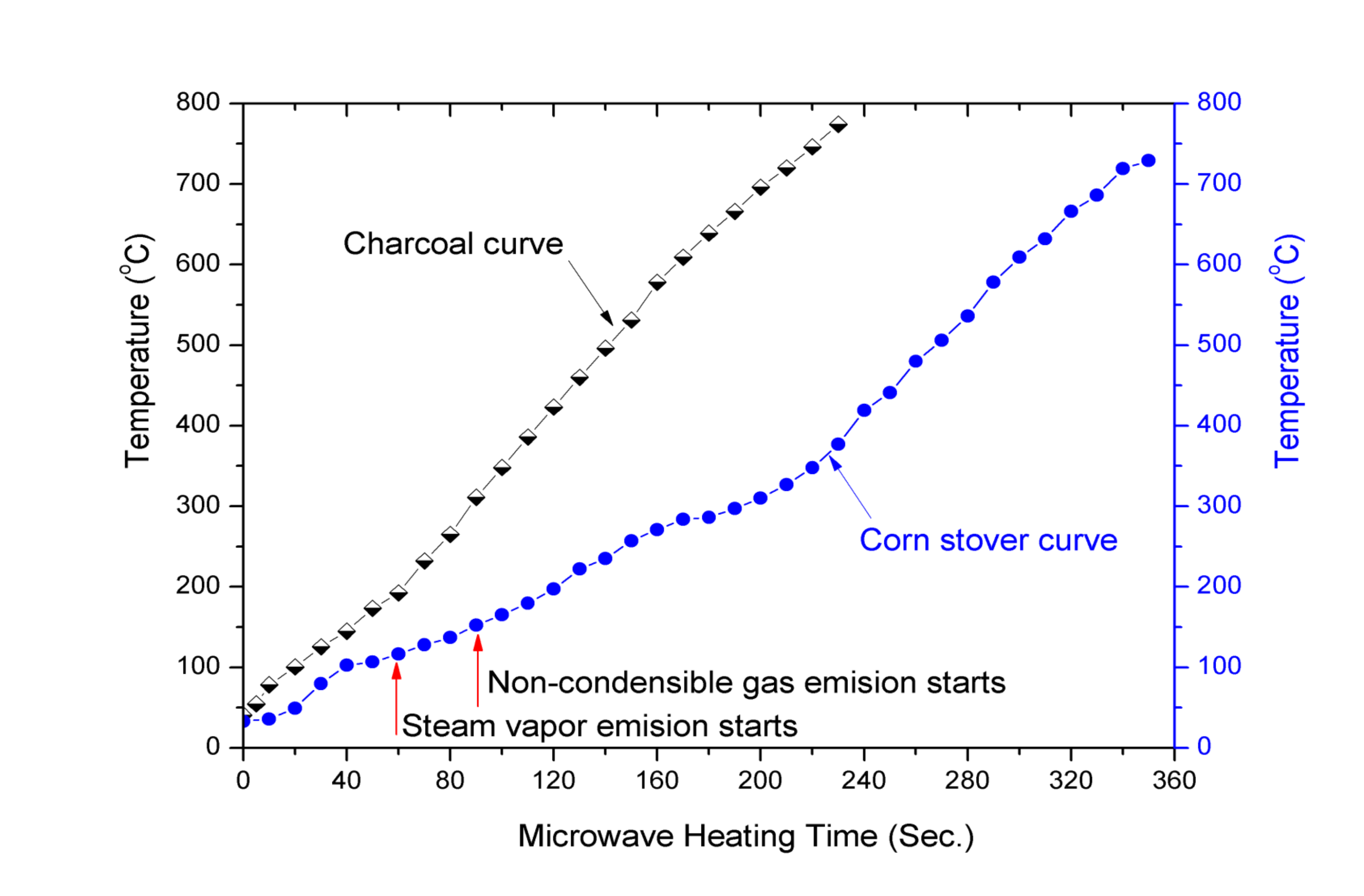


Municipal Solid Wastes

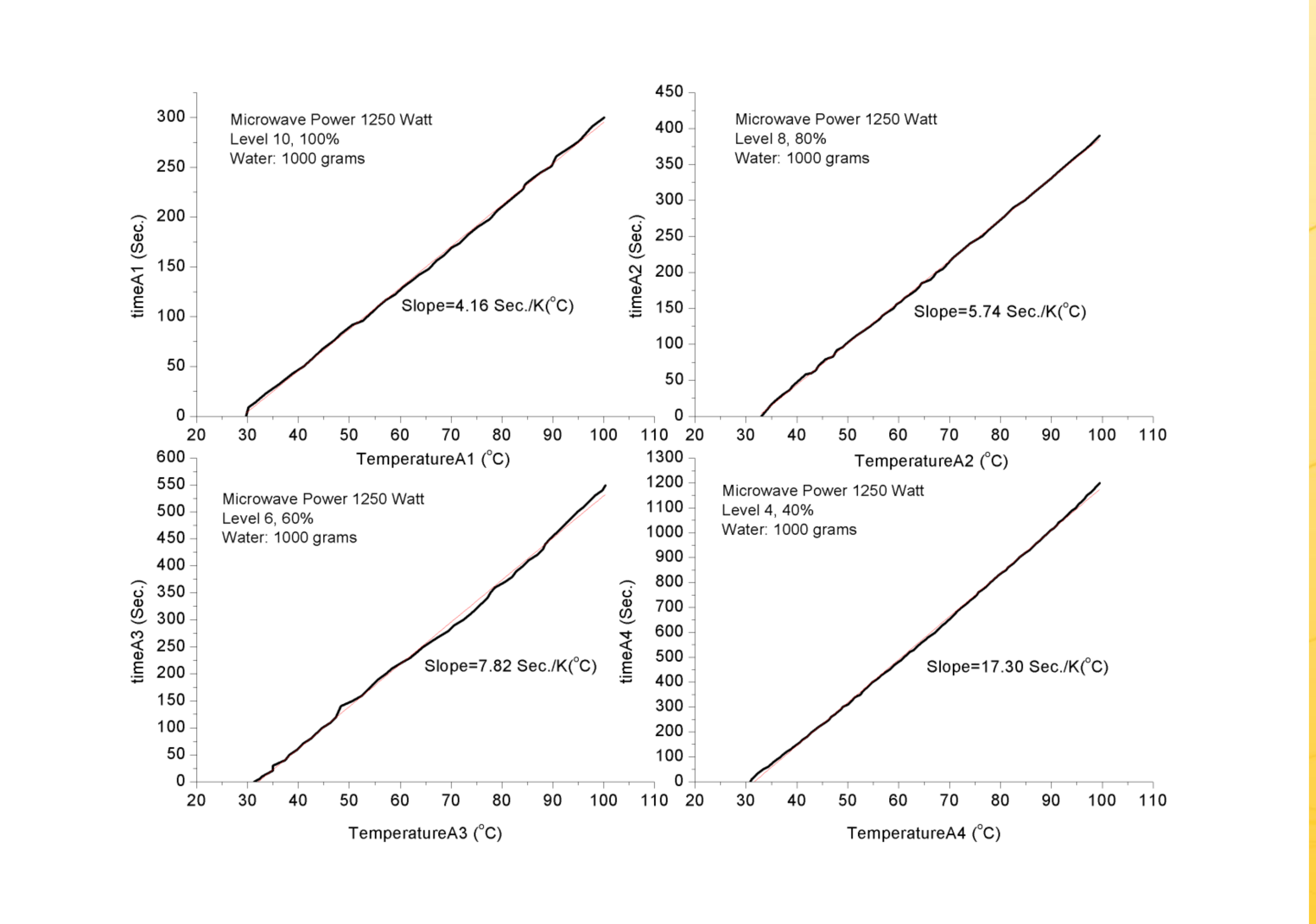
NNESOTA

MSW Pyrolysis Products

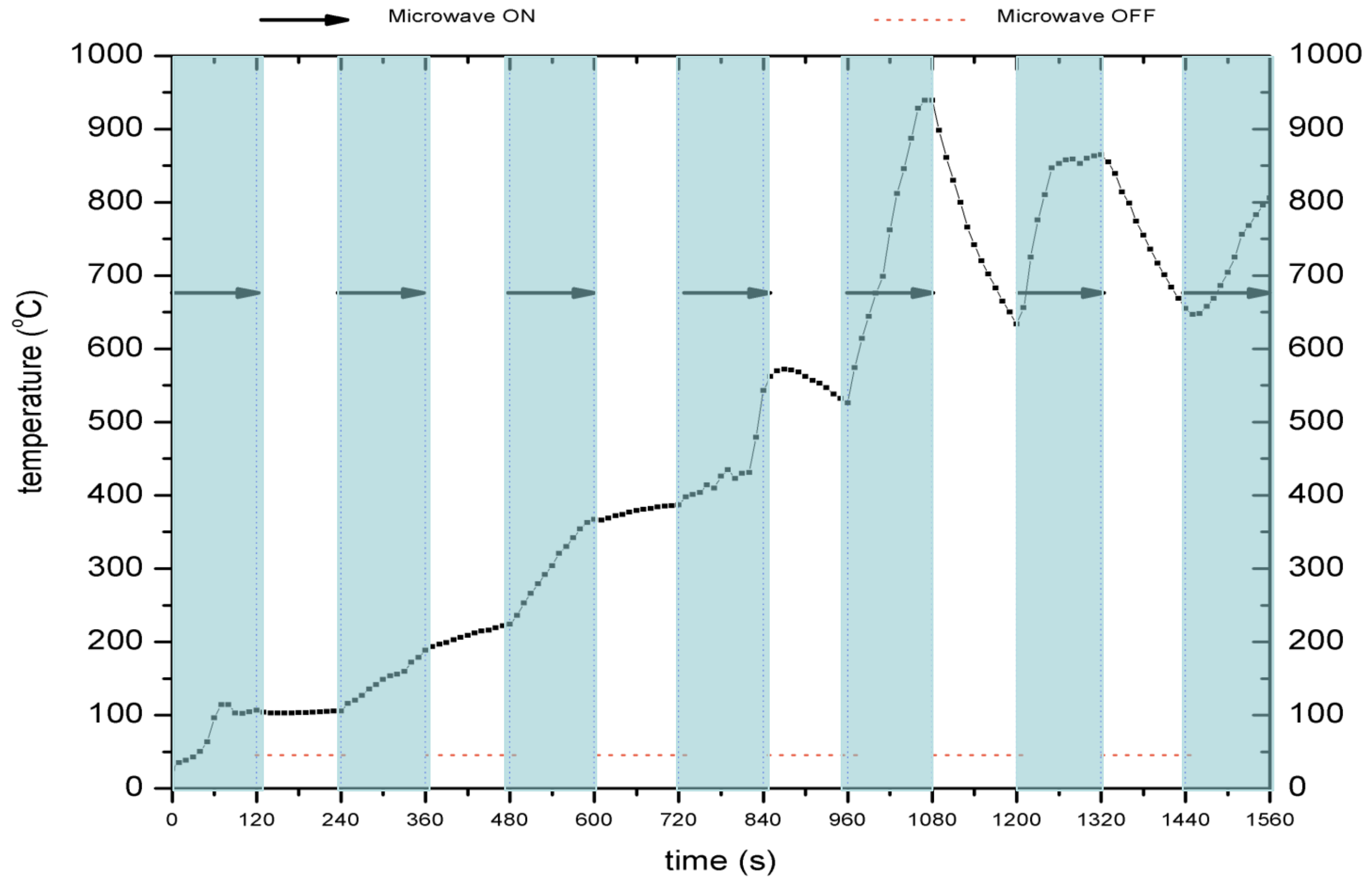
Microwave heating characteristics for different materials:



Power level calibration:



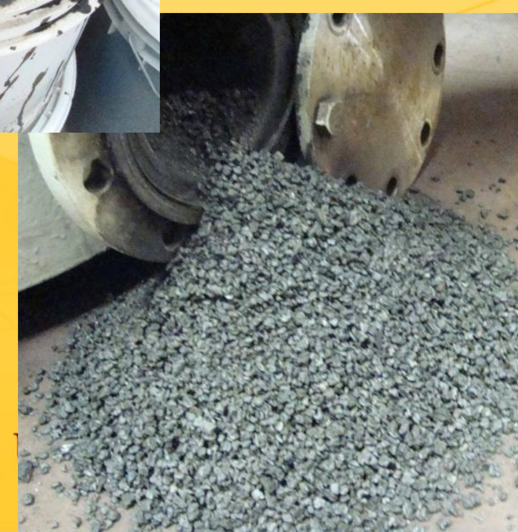
Temperature profile in MAP



Temperature profile of bulk corn stover during microwave-induced pyrolysis

Continuous microwave assisted pyrolysis system development


⚠ DANGER
HIGH TEMPERATURE
BIOOIL TANK
⚠ WARNING
⚠ DANGER
HIGH TEMPERATURE

Mobile Microwave Assisted Biomass Pyrolysis System

POPULAR SCIENCE

THE FUTURE NOW

OLD MACDONALD HAD A PYROLYSIS DOOHICKEY

Mobile biofuel refineries provide sustainable energy for farms

A hundred years ago, threshing machines chugged from farm to farm across the plains, separating stalk from grain and turning raw crops into valuable commodities. By sharing the machine, farmers could boost productivity without owning the prohibitively pricey equipment. Today, that business model could work for a new product: biofuel.

Biofuel from farm waste is a promising alternative to oil, but it's too expensive for any one farmer to make alone. Manufacturing cellulosic ethanol, the most common biofuel made from waste, costs up to $3 a gallon—going mostly to shipping raw materials and the enzymes used to break them down. Six years ago, Roger Ruan, a biosystems engineer at the University of Minnesota, began designing a smaller, simpler way to convert biomass to biofuel, using a process called pyrolysis.

The technique usually involves grinding biomass into a powder and heating it to break it into its chemical components, which are turned into fuel. The pulverizing ensures that the material heats evenly but is energy-hungry and slow. To eliminate the grinding step, Ruan added a microwave generator, which nukes chunks of organic material from the inside out. Off-the-shelf tech helps keep the price below that of conventional systems.

Ruan commissioned a Chinese factory to build a camper-size prototype, and this fall he'll hitch it to a pickup and hit the roads of rural Minnesota to conduct a field study. "We've got the choir signed on," says Linda Meschke, a Minnesota farmer who is lining up farms for the pilot study, "and a tentative congregation watching to see what happens next."

—MAGGIE KOERTH-BAKER

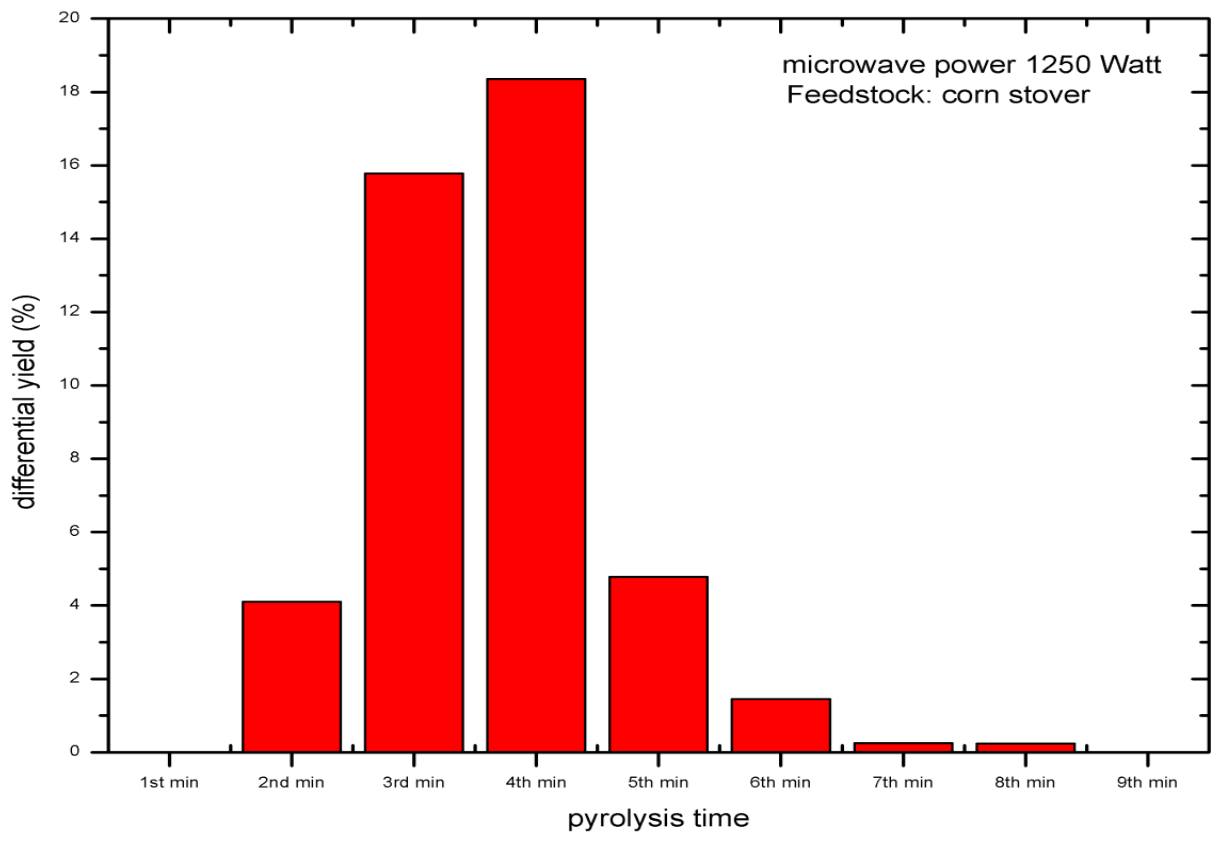
FILL 'ER UP

In one hour, this prototype biofuel maker could convert roughly 200 pounds of compost, trash, slaughter waste and other solids into fuel.

HOW TO TURN TRASH INTO POWER

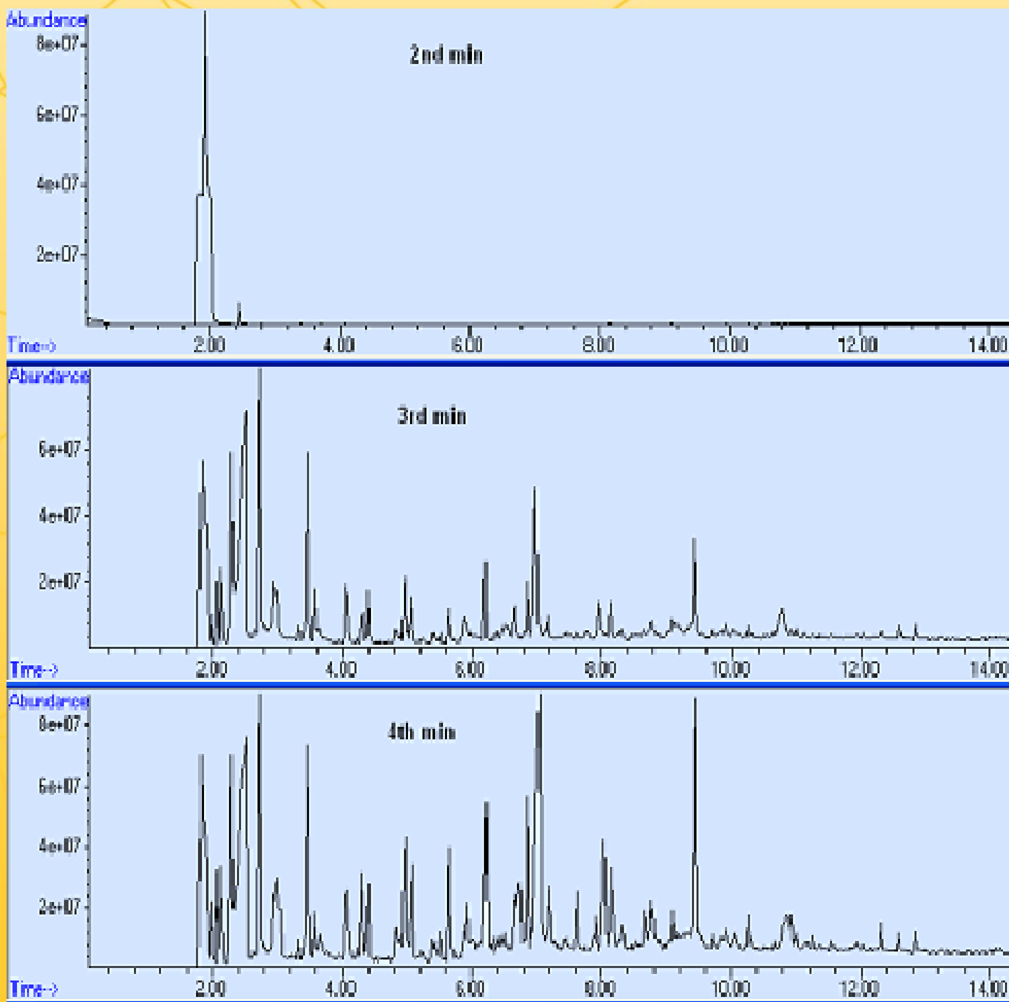
JUNE 11 The World Cup of soccer begins, featuring broadcasts in 3-D for the first time. Put on your special glasses and tune in to ESPN to watch up to 25 3-D matches.

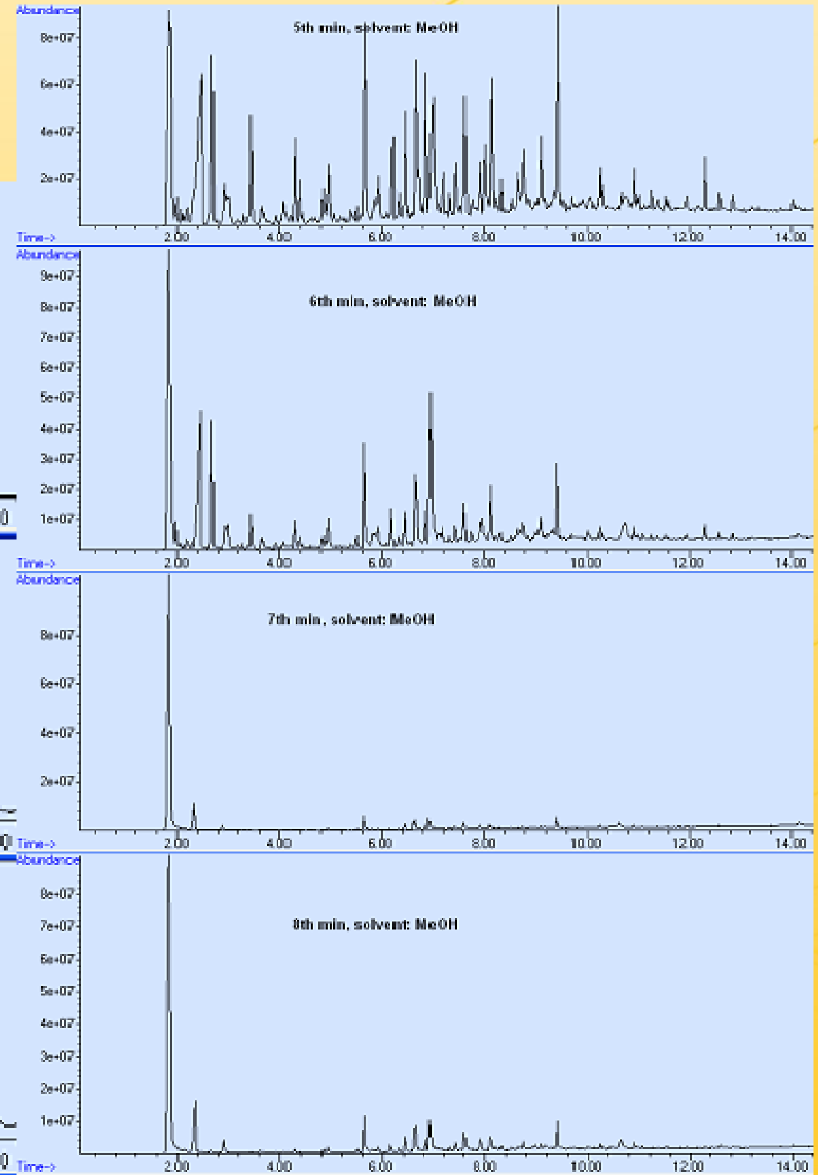
Pyrolytic biooil differential yields



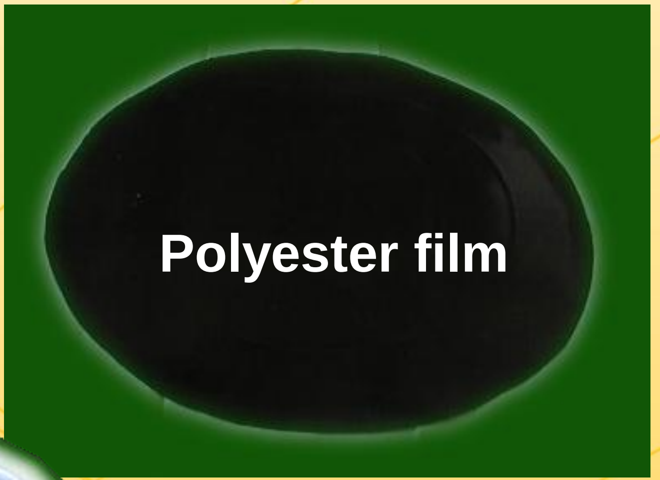
Retention time effect in MAP

Feedstock: Corn Stover, Power level:1250 Watt
GC-MS analysis





Biorefining of Biooils and Liquefied Biomass

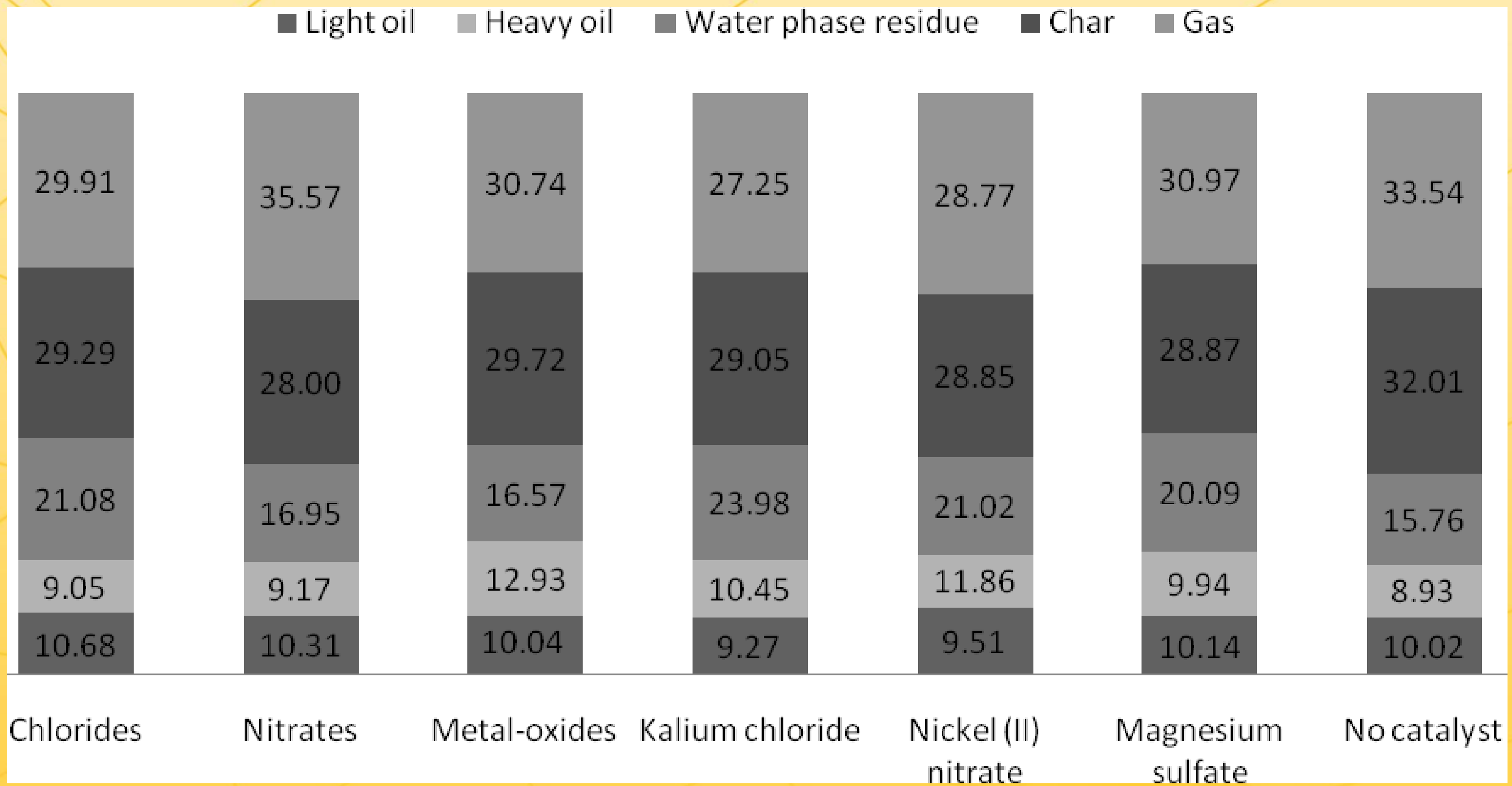


Polyurethane foam

Wood Adhesive

Biofuel

Catalytic pyrolysis



Pyrolysis fraction yields (mass% of total biomass input) from runs with different catalysts and catalyst groups added to the **aspen** pellets

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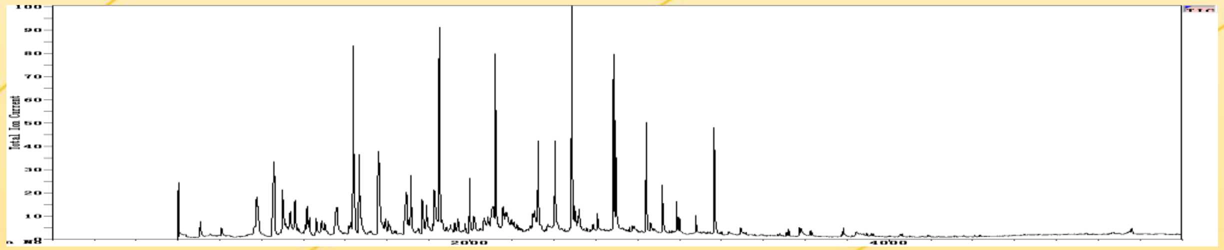
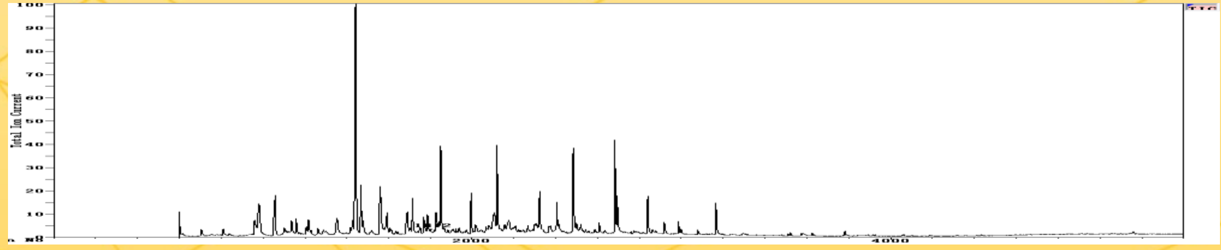
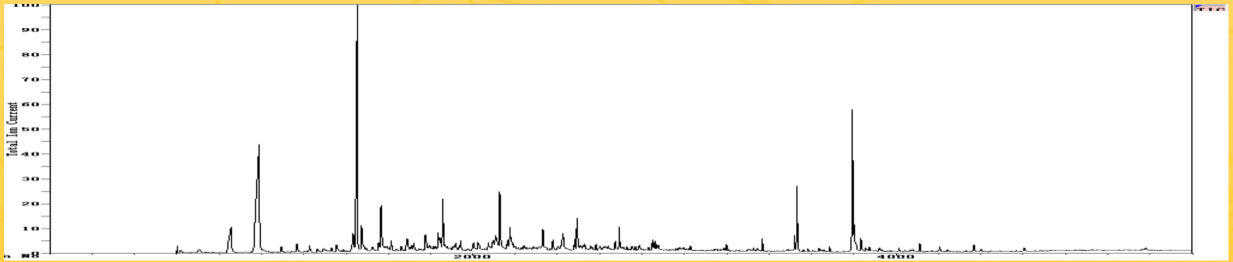
Typical Compositions by Nitrates such as $(MgNO_3)_2$, $Fe(NO_3)_3$



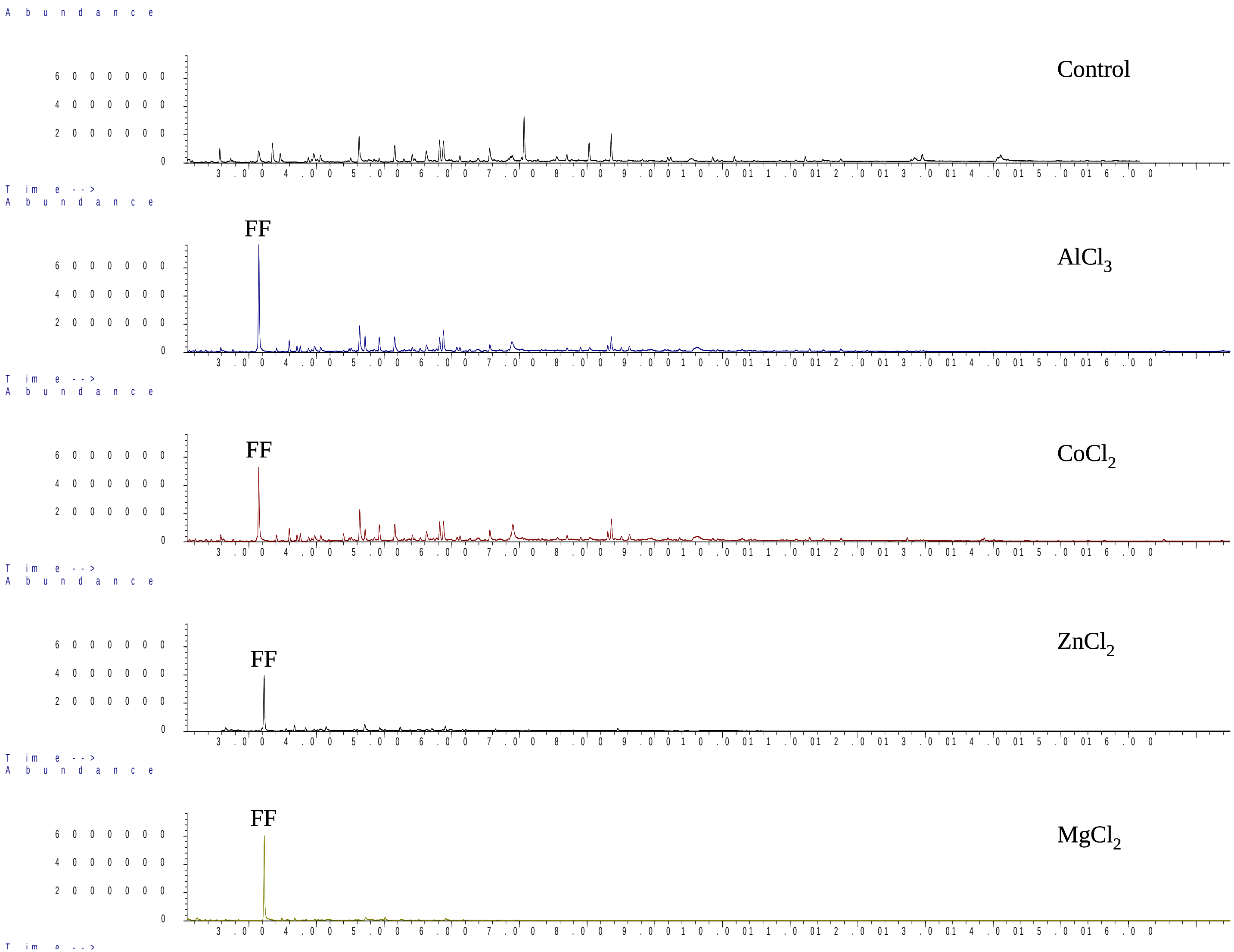
Typical Compositions by Sulfates such as Na_2SO_4, $MgSO_4$



Typical Compositions by Chlorides such as $AlCl_3$, $MgCl_2$, $ZnCl_2$ and $FeCl_3$



Chlorides help to improve and simplify the composition of bio-oil, compared with nitrates and sulfates.



Total ion chromatograms from GC-MS analysis of pyrolytic oils from corn stover when different catalysts were used (8g/100g biomass). FF: furfural.

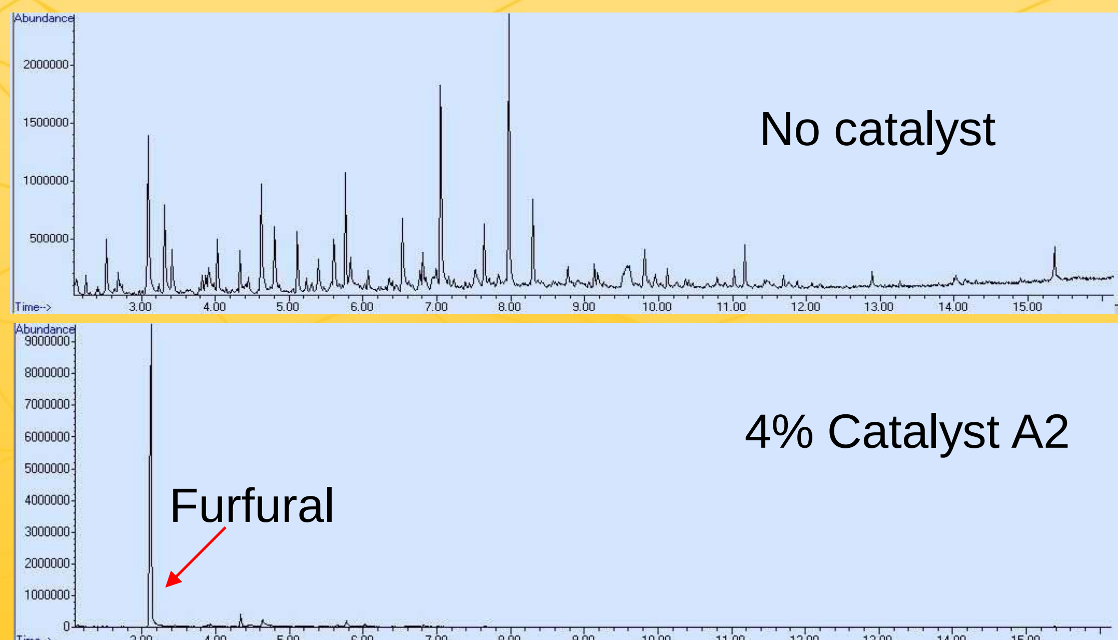
Microwave Pyrolysis in a Continuous System

Effect of temperature and catalyst on products (Dry basis)

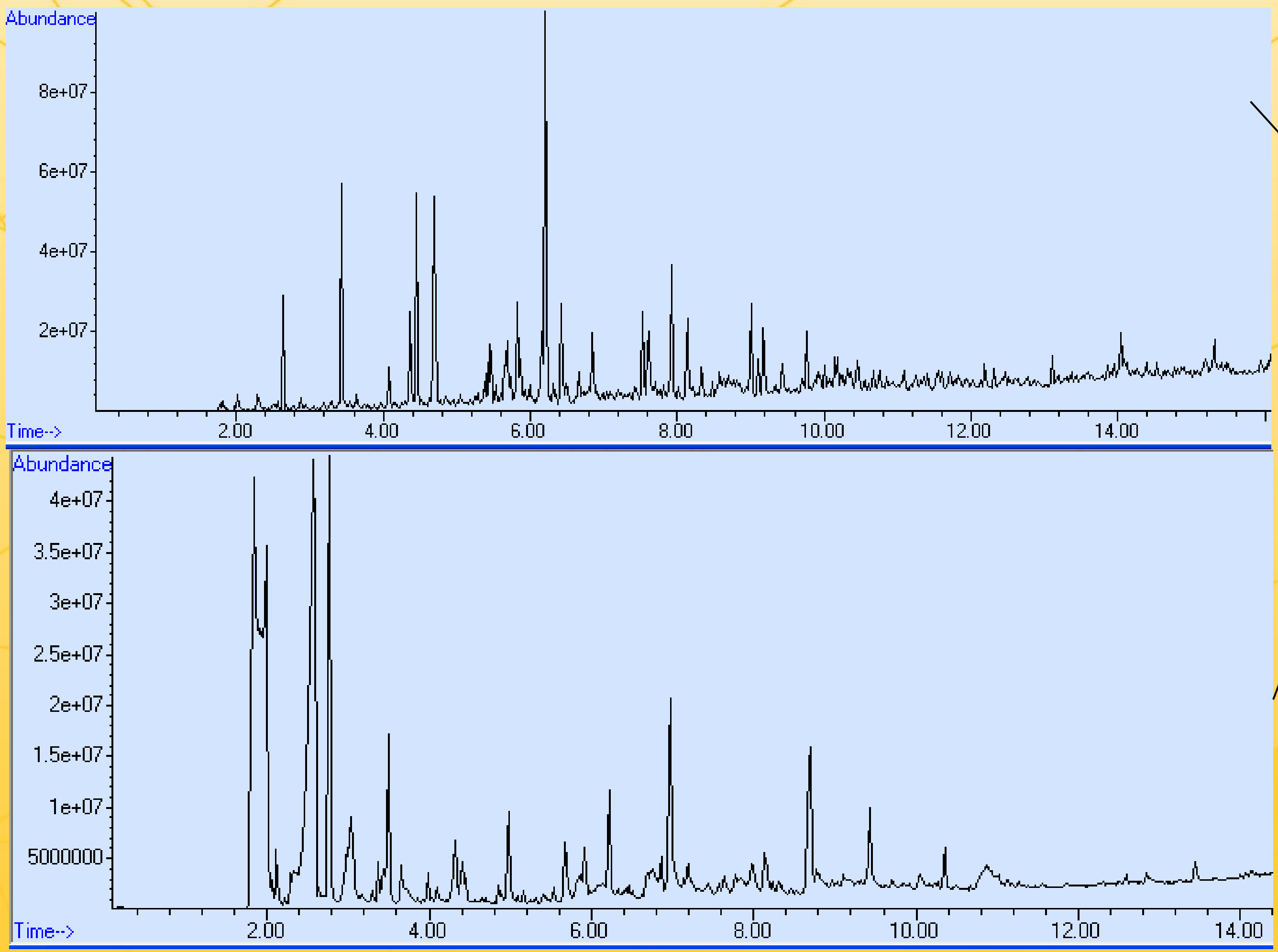
Temperature /^{o}C	Catalyst	Bio-oil /%	Char /%	Gas /%
475	-	42.0	35.1	22.9
375	-	39.6	38.9	21.5
325	-	38.5	43.6	17.9
375	Catalyst A2	38.8	41.3	19.9

Sample: Corn cob
Feeding rate: 20Kg/h
Size: <1.2cm

Addition of catalyst A2 helps corn cob pyrolysis to produce a chemical-furfural.



Co-pyrolysis of corn stover and scrap tire



Phase separation!

Top phase

Bottom phase

Corn stover : tire = 1:1


Sun Dried Algae

Comparison of fossil oil and bio-oils from MAP of *Chlorella* sp. algae and wood

Properties	Bio-oils: *Chlorella* sp.	Bio-oils: Wood[a]	Fossil oil[a]
Elemental analysis (wt.%)			
C	65.40	56.4	83.0-87.0
H	7.84	6.2	10.0-14.0
N	10.28	0.1	0.01-0.7
O	16.48[b]	37.3	0.05-1.5
HHV (MJ/kg)	30.7[c]	21	42
Density (kg/L)	0.98[d]	1.2	0.75-1.0
Viscosity, at 40 ^{o}C (Pa s)	0.06	0.04-0.20	2-1000
pH	7-9.5	2.5-3	

Elemental composition of algae bio-oil

Sample Info:

Client Name:	New Generation Biofuels
Sample Description:	Algae Biodiesel
NABL Identification #:	10-140

Test Conditions

Date Analyzed:	Sept 15 2010
Instrument:	CE Elantech FlashEA 1112 CHNS/O Analyzer
Reference Standard:	BBOT

Results

%Carbon:	64.12032318
%Hydrogen:	8.272509257
%Nitrogen	9.7
%Sulfur:	0
%Oxygen:	12.01842054

Data Interpretation

% Composition accounted for:	94.11125298
Compound formula: Carbon	5.343
Hydrogen	8.205
Nitrogen	0.693
Sulfur	0.000
Oxygen:	0.751

Algae bio-oil and blend

NABL ID #	Test Description	Test ID / Method	Result
10-140	pH	A23 / SOP 4-4-01-A23	8.37
10-140	Sulfated Ash	F6 / ASTM D874	0.0088% ♦
10-140	Kinematic Viscosity @ 40°C*	A5 / ASTM D445	45.57 cSt
10-140	Flash Point (Cleveland Open Cup)*	A1 / ASTM D92	80°C ▼
10-140	Pour Point*	A32 / ASTM D6749	-13°C
10-140	Carbon Residue	F10 / ASTM 4530	8.22%
10-140	Ultimate Analysis (CHONS)		See attached sheet
10-140	Specific Gravity @ 15.5°C/60°F	A40 / ASTM D1298	1.029
10-140	Gross Heat of Combustion	A51 / ASTM D240	30.43 MJ/kg
AN 10850	Water and Sediment	F9 / ASTM D2709	Δ
AN 10850	pH	A23 / SOP 4-4-01-A23	8.26
AN 10850	Sulfated Ash	F6 / ASTM D874	0.0096% ♦
AN 10850	Kinematic Viscosity @ 40°C*	A5 / ASTM D445	46.95 cSt
AN 10850	Flash Point (Cleveland Open Cup)*	A1 / ASTM D92	100°C ▼
AN 10850	Pour Point*	A32 / ASTM D6749	-14°C
AN 10850	Carbon Residue	F10 / ASTM 4530	5.40%
AN 10850	Ultimate Analysis (CHONS)		See attached sheet
AN 10850	Specific Gravity @ 15.5°C/60°F	A40 / ASTM D1298	1.027
AN 10850	Gross Heat of Combustion	A51 / ASTM D240	23.51 MJ/Kg

Hydrothermal pretreatment

- Reduce nitrogen contents in algal feedstock by hydrolysis of protein; reduce energy inputs required for algae dewatering and drying.

Algae Slurry

Reactor

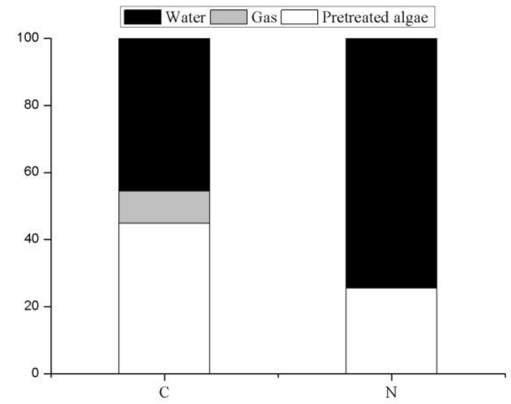
Sand Bath

Continuous Hydrothermal Biomass Pyrolysis System

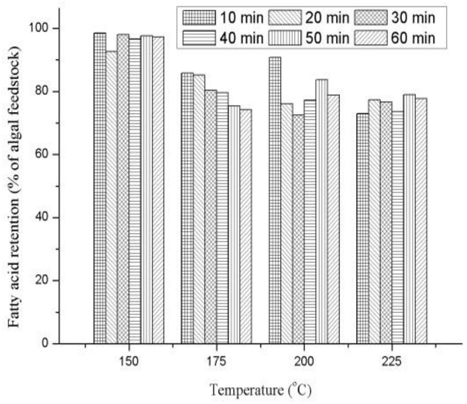
High Throughput Continuous Catalytic Hydrothermal Conversion System

			Elemental composition (%)						HHV(MJ/kg)
			C	H	N	Ash	C retention	N retention	
Untreated algae			39.9	5.5	6.2	24.4			16.8
Pretreated algae	Temperature (°C)	Time (min)							
	150	10	51.0	7.0	8.3	14.4	81.6	84.9	21.7
		20	51.0	7.0	8.0	14.3	83.9	84.5	21.7
		30	51.1	6.9	7.8	12.4	74.3	73.0	21.7
		40	50.5	6.9	7.7	14.7	77.7	76.2	21.4
		50	51.3	7.0	7.7	14.6	75.9	73.1	21.8
		60	52.0	7.0	7.6	12.8	77.8	73.2	22.1
	175	10	49.9	6.9	7.0	18.8	64.0	57.8	21.0
		20	52.7	7.2	6.7	17.2	60.7	49.5	22.4
		30	53.1	7.2	6.5	14.3	56.8	44.9	22.7
		40	54.8	7.4	6.1	14.0	58.8	42.0	23.6
		50	54.6	7.3	6.0	14.8	58.6	41.1	23.4
		60	53.7	7.1	6.2	14.0	56.7	42.4	22.9
	200	10	49.1	6.6	6.6	22.1	55.7	48.3	20.5
		20	54.0	7.1	5.7	16.7	49.5	33.5	23.0
		30	51.1	6.8	5.8	19.9	48.4	35.1	21.4
		40	57.5	7.6	5.1	13.6	44.8	25.7	25.1
		50	56.9	7.6	4.8	13.5	43.8	23.9	24.7
		60	54.4	7.2	5.1	12.8	43.4	26.0	23.1
	225	10	51.1	6.8	6.1	18.8	45.8	34.9	21.4
		20	58.2	7.7	5.4	13.9	45.9	27.1	25.6
		30	58.7	7.8	4.8	13.6	42.9	22.5	25.9
		40	63.6	8.3	4.8	12.8	43.8	21.3	29.4
		50	63.1	8.1	4.4	12.2	43.3	19.2	28.8
		60	67.5	9.1	3.6	13.5	39.6	13.4	32.7

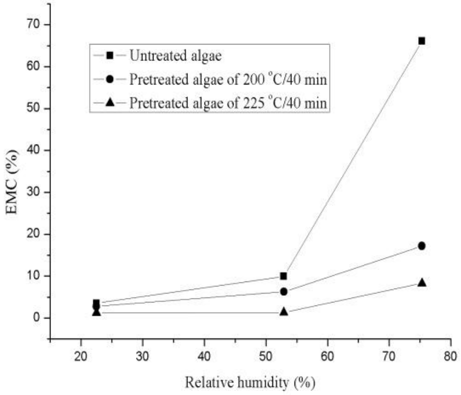
Pretreated algae samples had higher carbon contents and enhanced heating values under all reaction conditions and N removal of over 75% at 200 °C−225 °C for 30−60 min.



C and N distribution among the products of HP under 200 °C, 40 min condition.



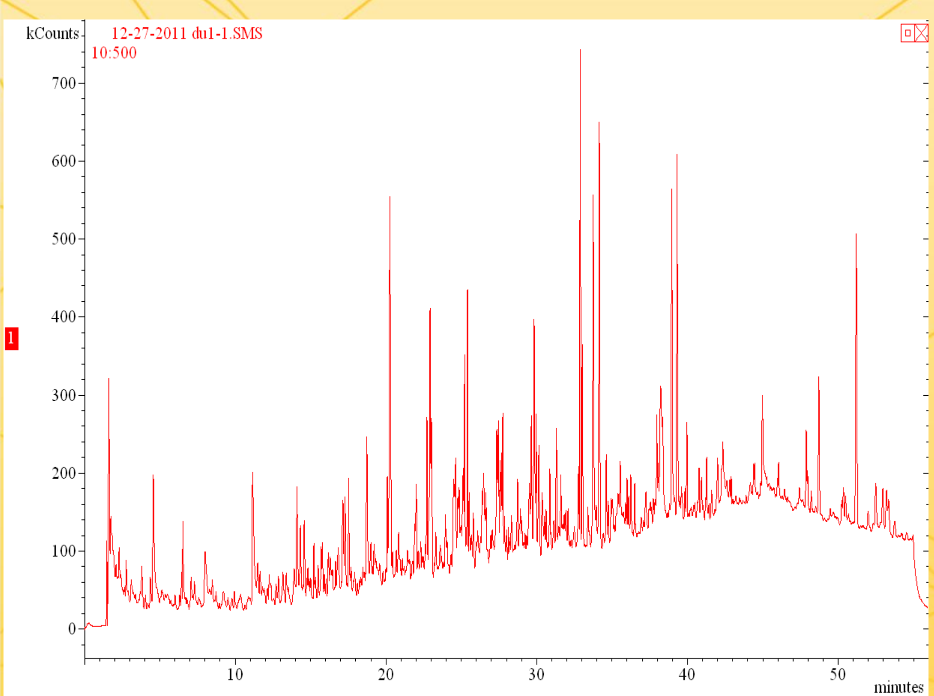
Fatty acid retention in pretreated



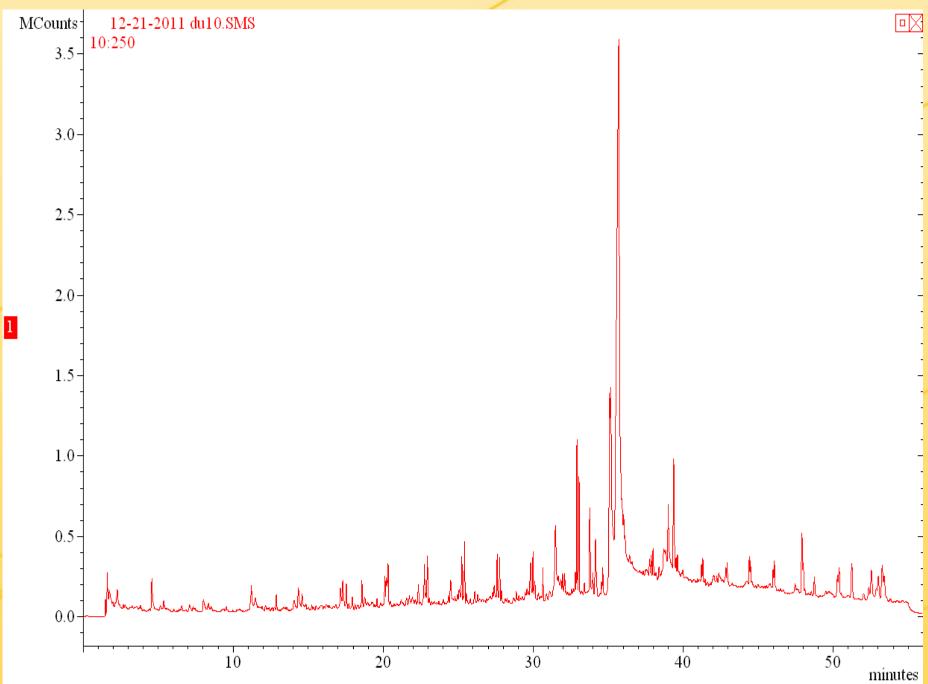
EMC of untreated and pretreated algae.

- 75% of N removal was achieved.
- 73%-99% of fatty acids retention was obtained, which means very minor amount of lipids loss during pretreatment.
- Pretreated algae were more hydrophobic, had much lower water holding capacity, and were much easier to be dried and stored with less biological deterioration

GC-MS profiles of bio-oils from untreated and pretreated algae



raw microalgae



pretreated microalgae

The pyrolytic bio-oil from pretreated algae contained less N-containing compounds and the bio-oil contained mainly long-chain fatty acids (C14−C18, over 45%) which can be more readily converted into hydrocarbon fuels in the presence of simple catalysts.

Wastewater to algae to biofuels system

University of Minnesota

- **Acquire Commercially Available Catalysts**
- **Acquire Raw Materials for Making Biorefining Catalysts**
- **Synthesize Biorefining Catalysts**
  - Hydrotreating/Hydrocracking Catalysts
  - Metathesis Catalysts

Acquire/Catalysts Synthesis

Catalyst Used for Bio-oil Conversion

Catalysts Synthesis

	
Zeolite Precursor Synthesis	Zeolite Precursor Synthesis

Catalyst Screening Microreactor Setup

University of Minnesota

Center for Biorefining

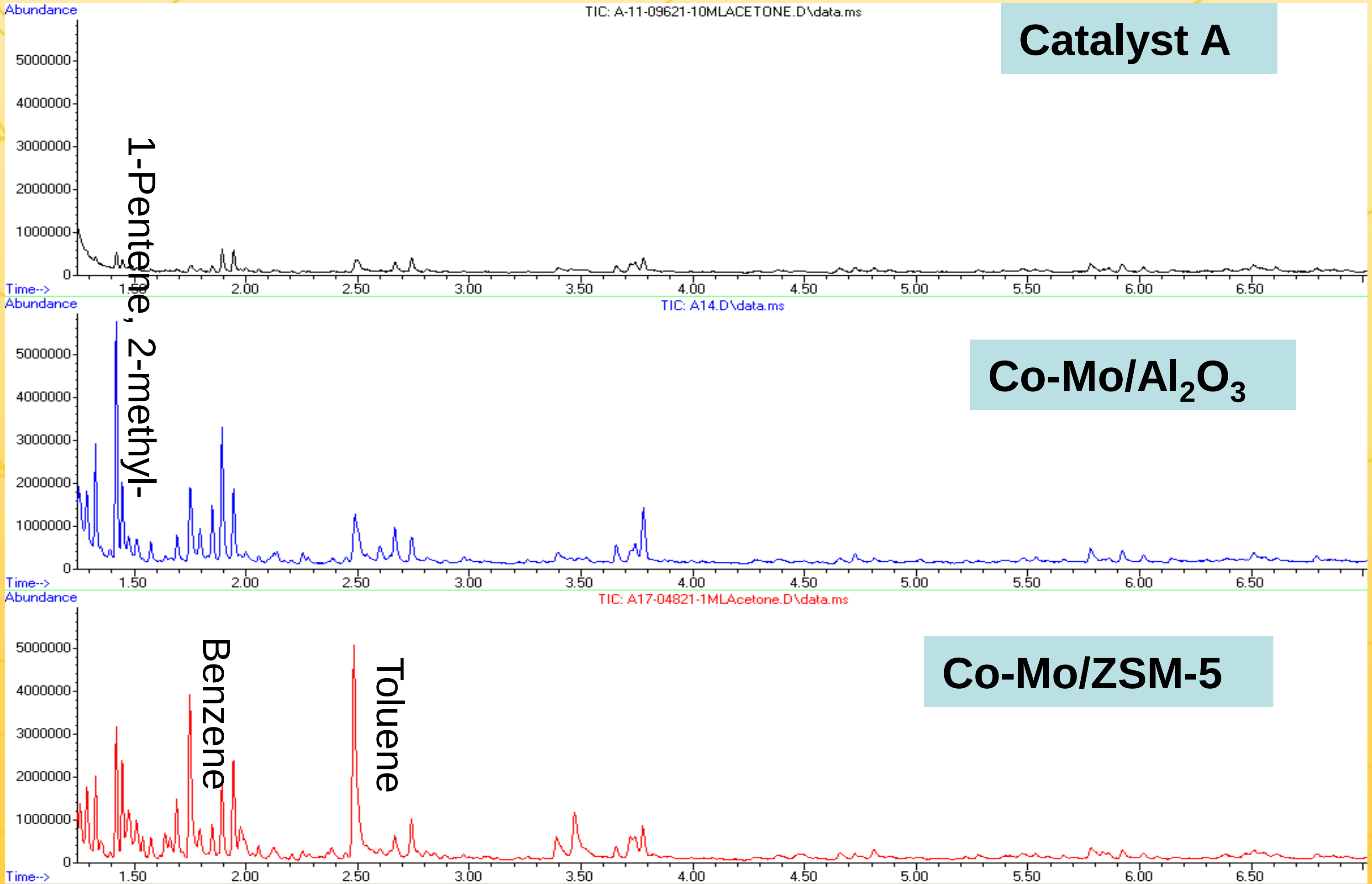
Pressurized hydro-processing system

UNIVERSITY OF MINNESOTA
Center for Biorefining

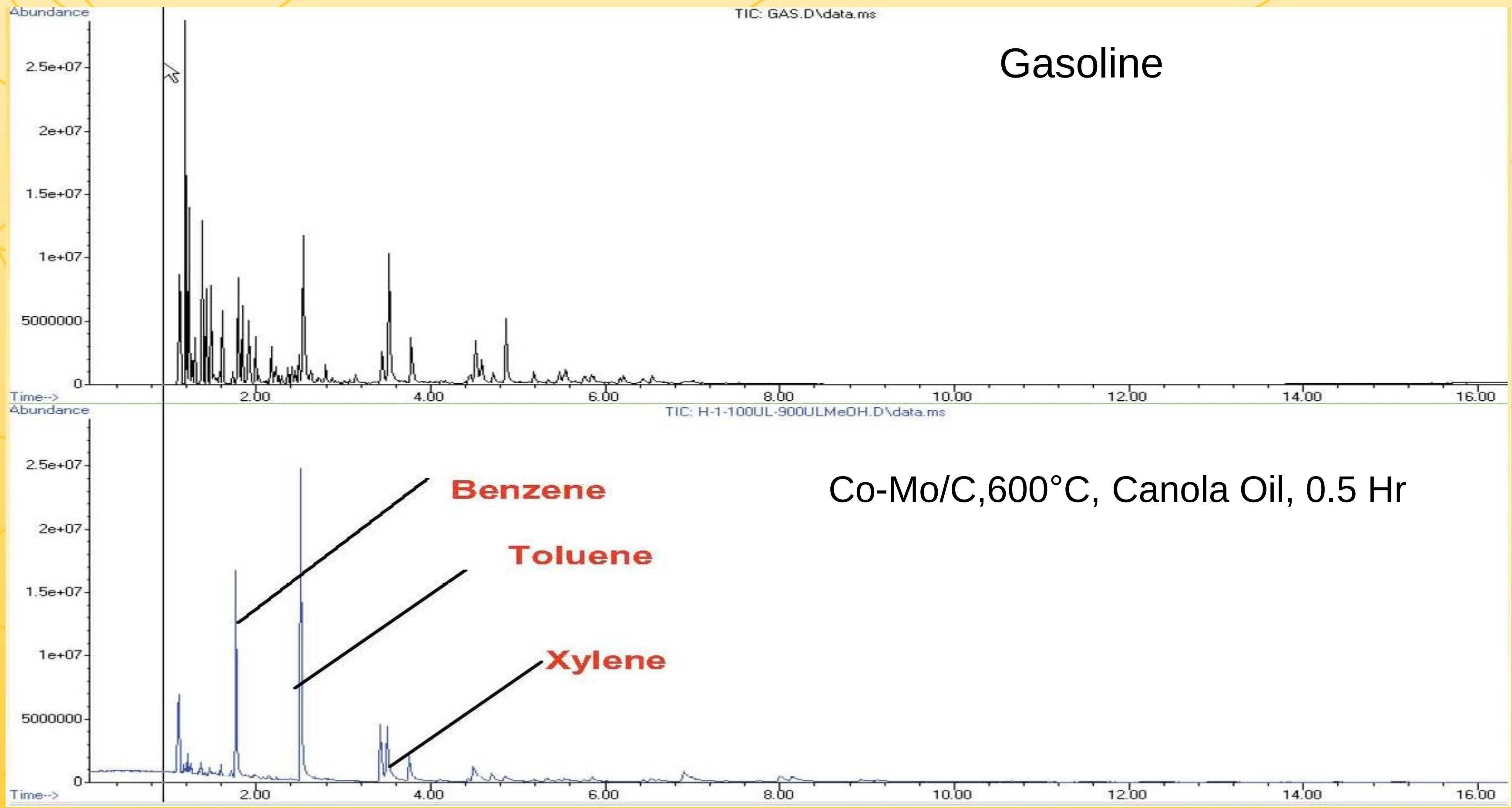
Catalyst Used for Bio-oil Conversion

Catalyst A	Catalyst B	Catalyst C	Catalyst D
Ni-Ru/ Al_2O_3(self-prepared)	Ni-Co/C (self-prepared)	CBV-400 (Zeolyst International)	CBV-780 (Zeolyst International)
Catalyst E	Catalyst F	Catalyst G	Catalyst H
Ni/Alumina/Silica	Al_2O_3	Zeolite mixed with Al_2O_3	Cu-CBV 400 (Self prepared)

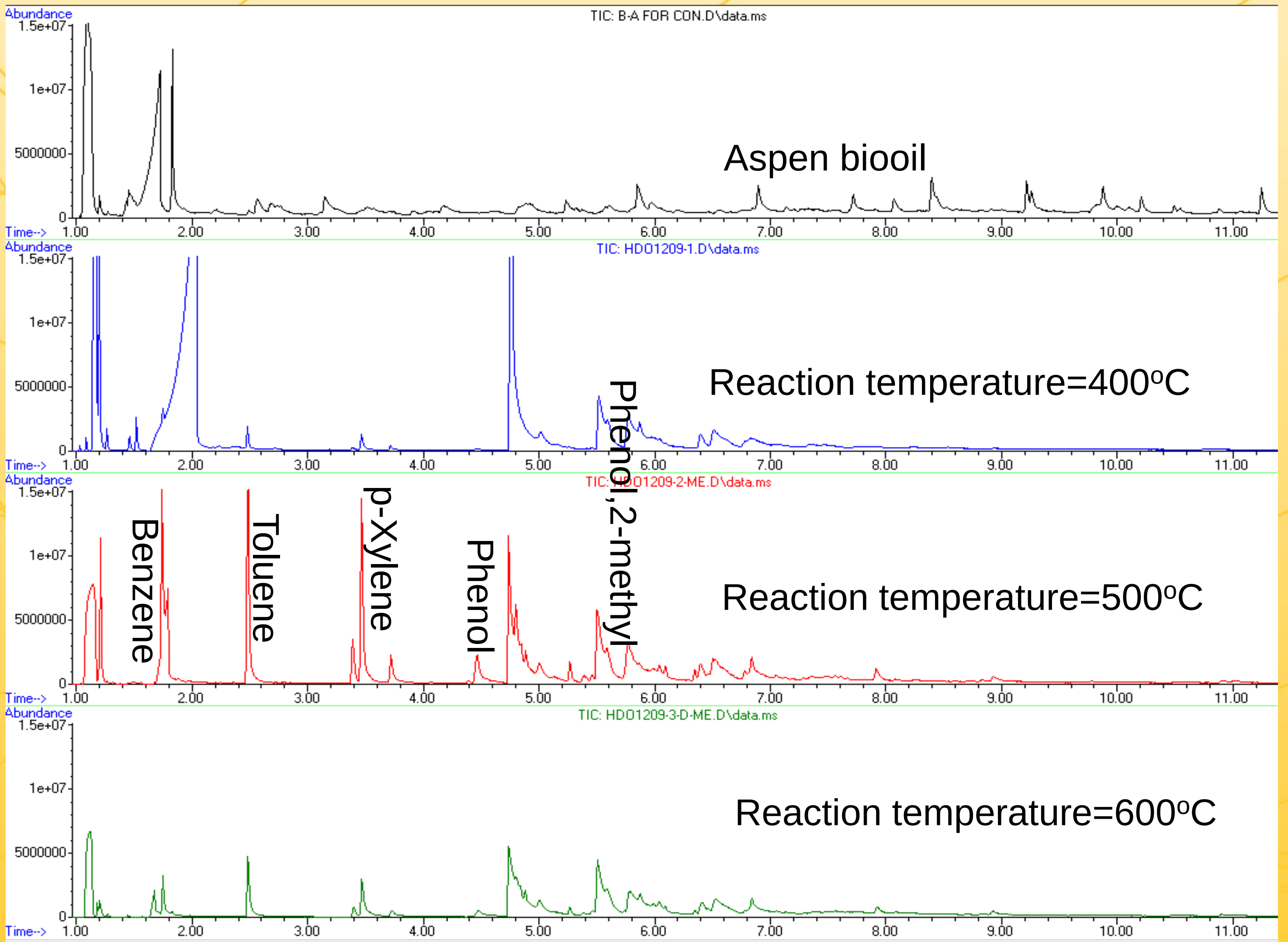
Canola oil with catalysts



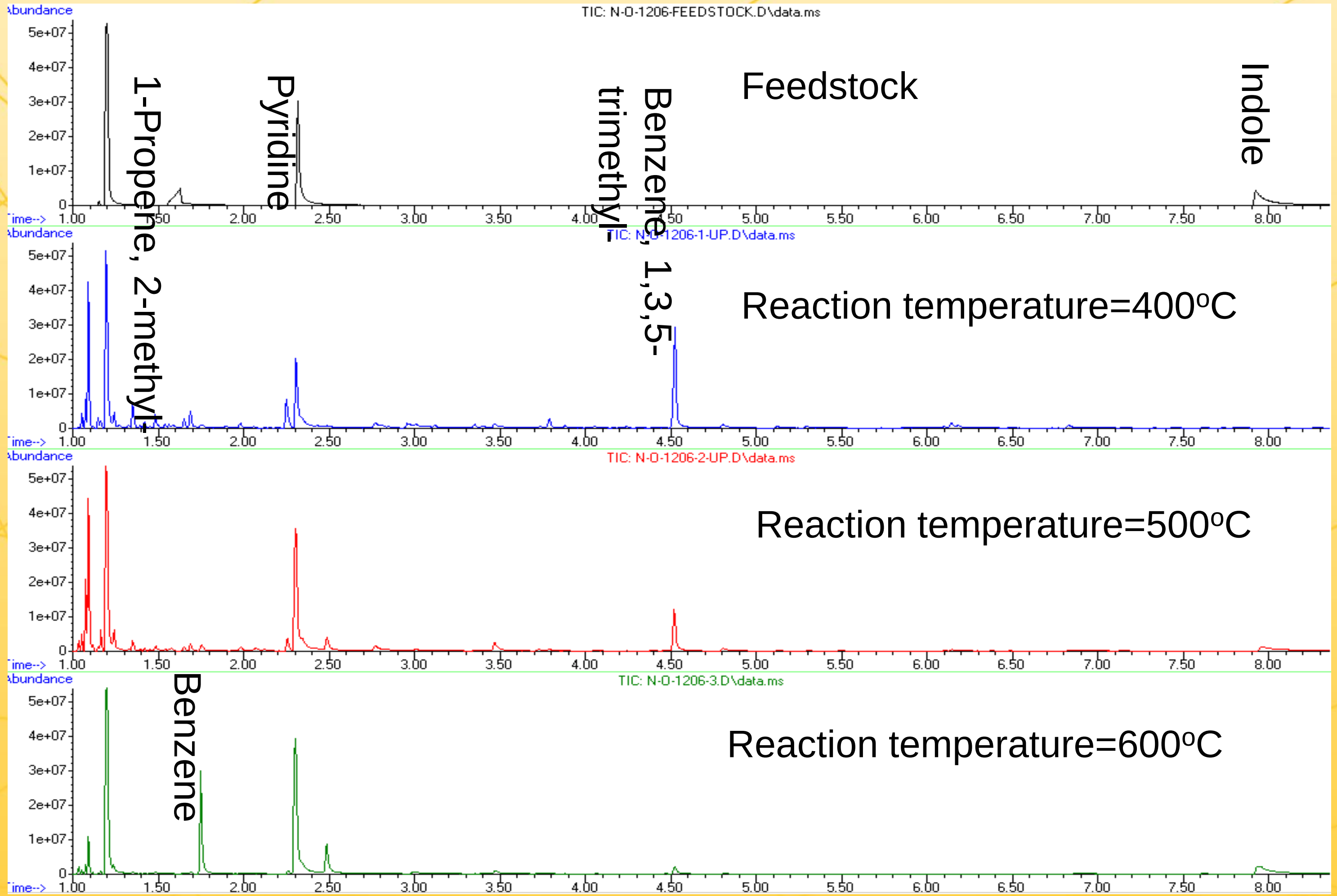
Hydrotreating Canola oil



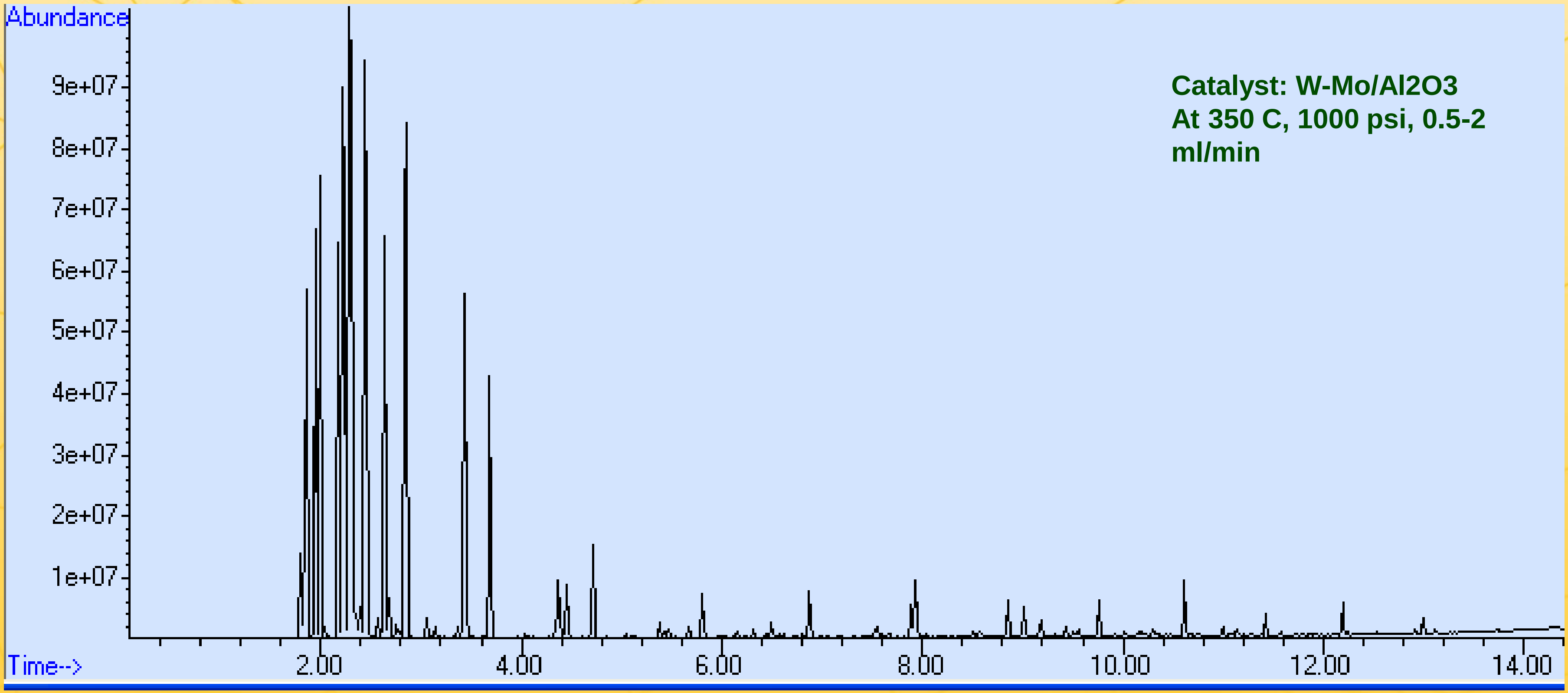
HDO of wood derived oil



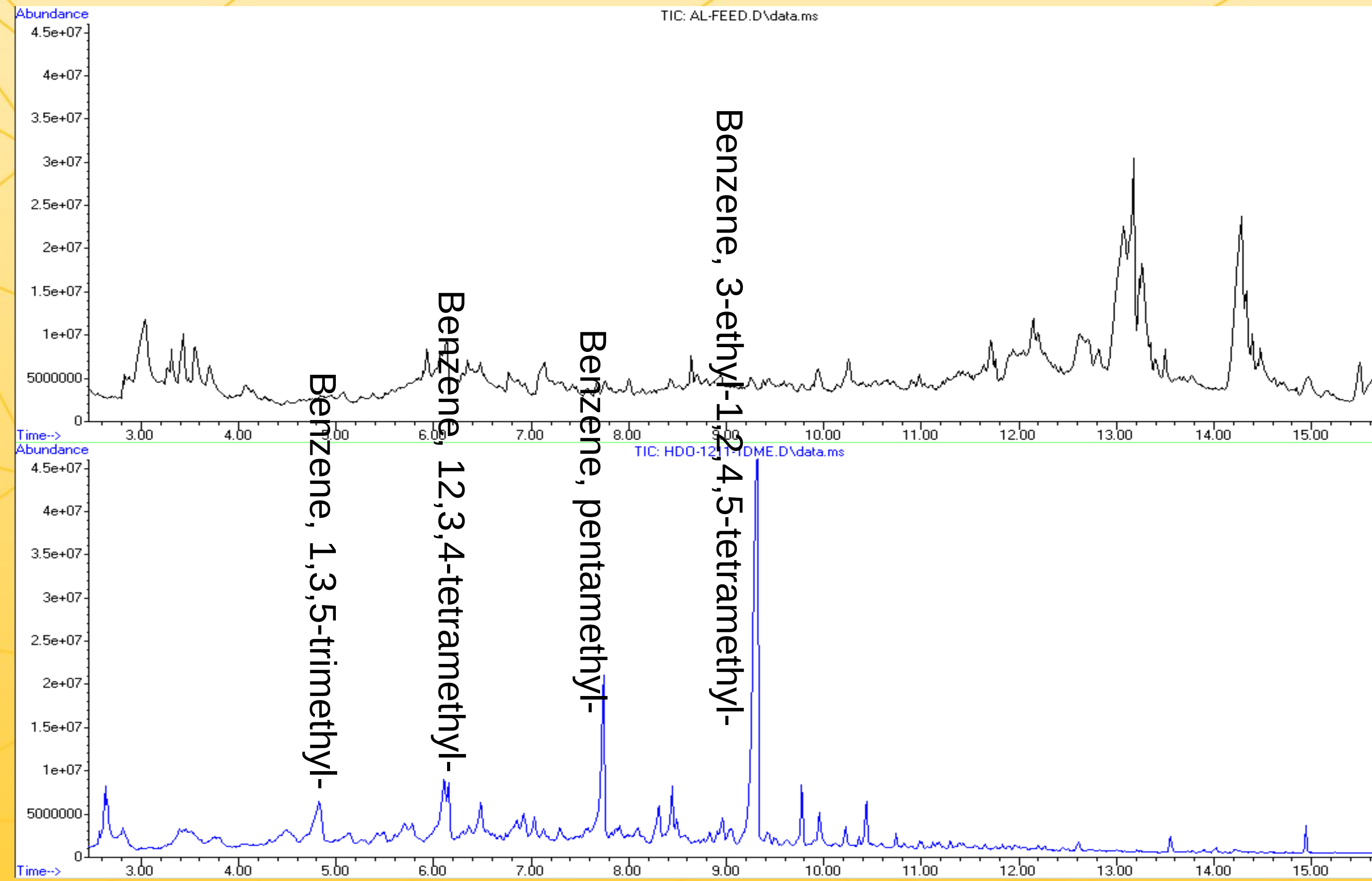
HDN/HDO of N-O containing compound



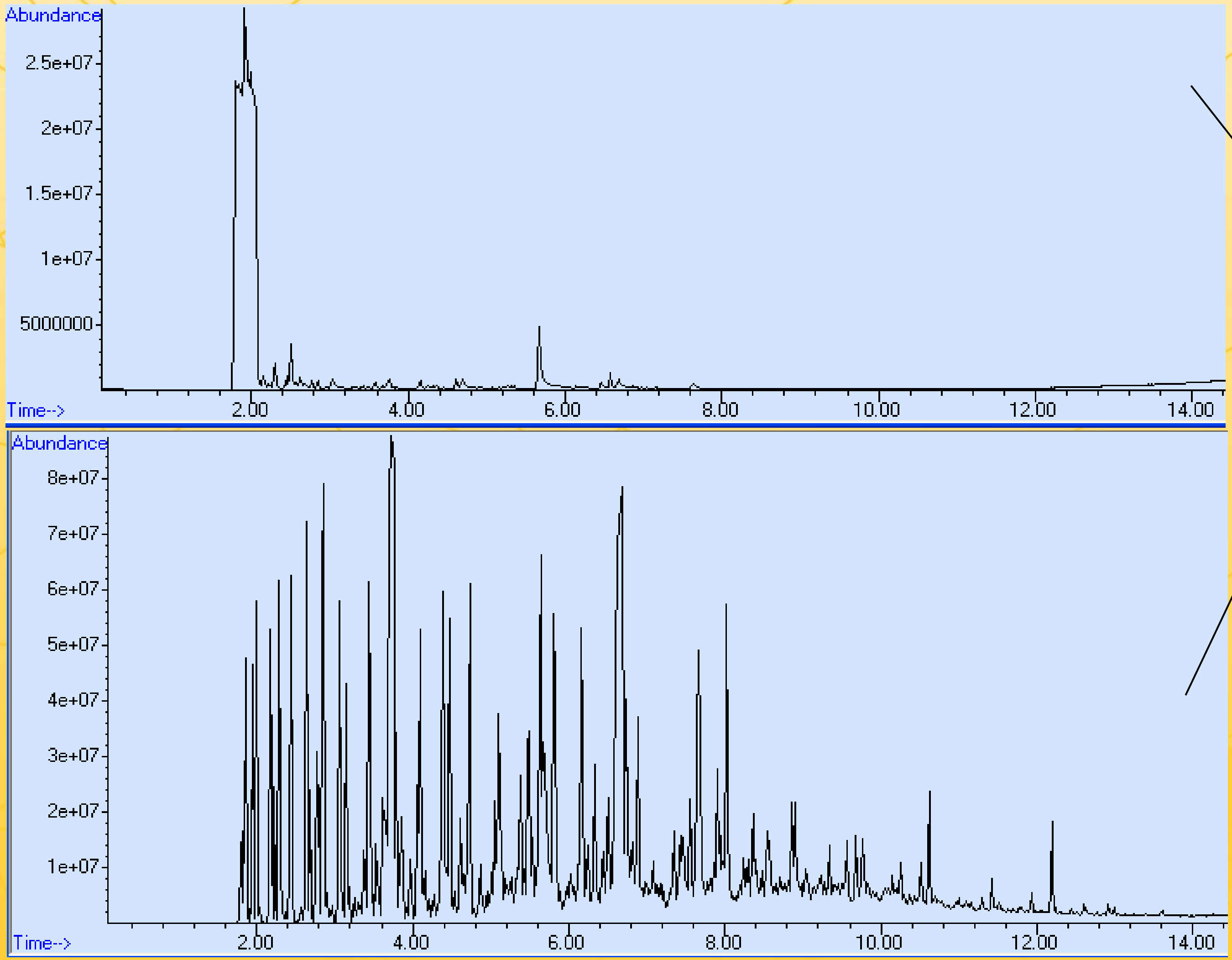
Hydrogenation of algal pyrolytic biooil



HDO/HDN of algae derived oil



Catalytic upgrading



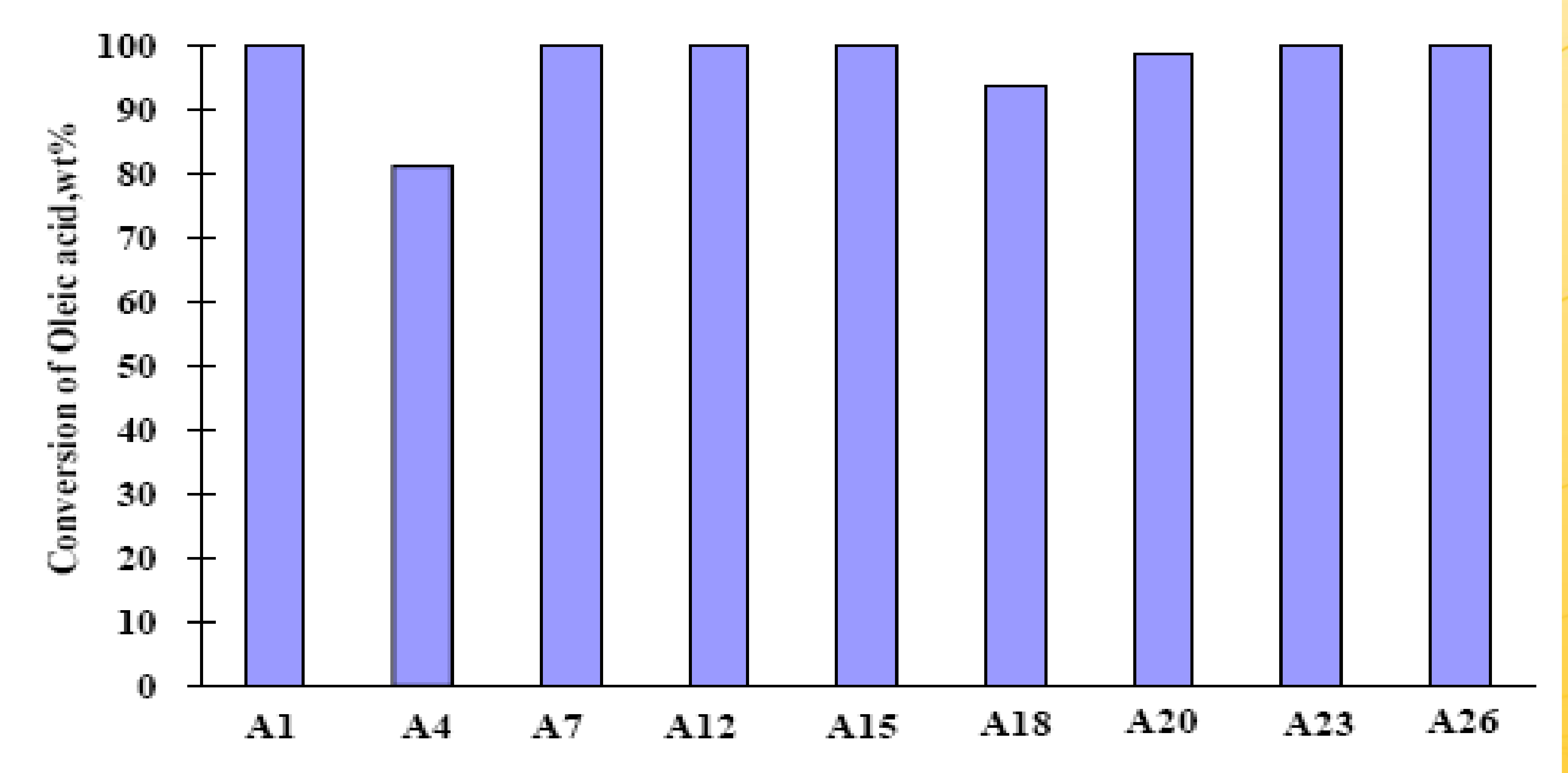
Top phase

Bottom phase

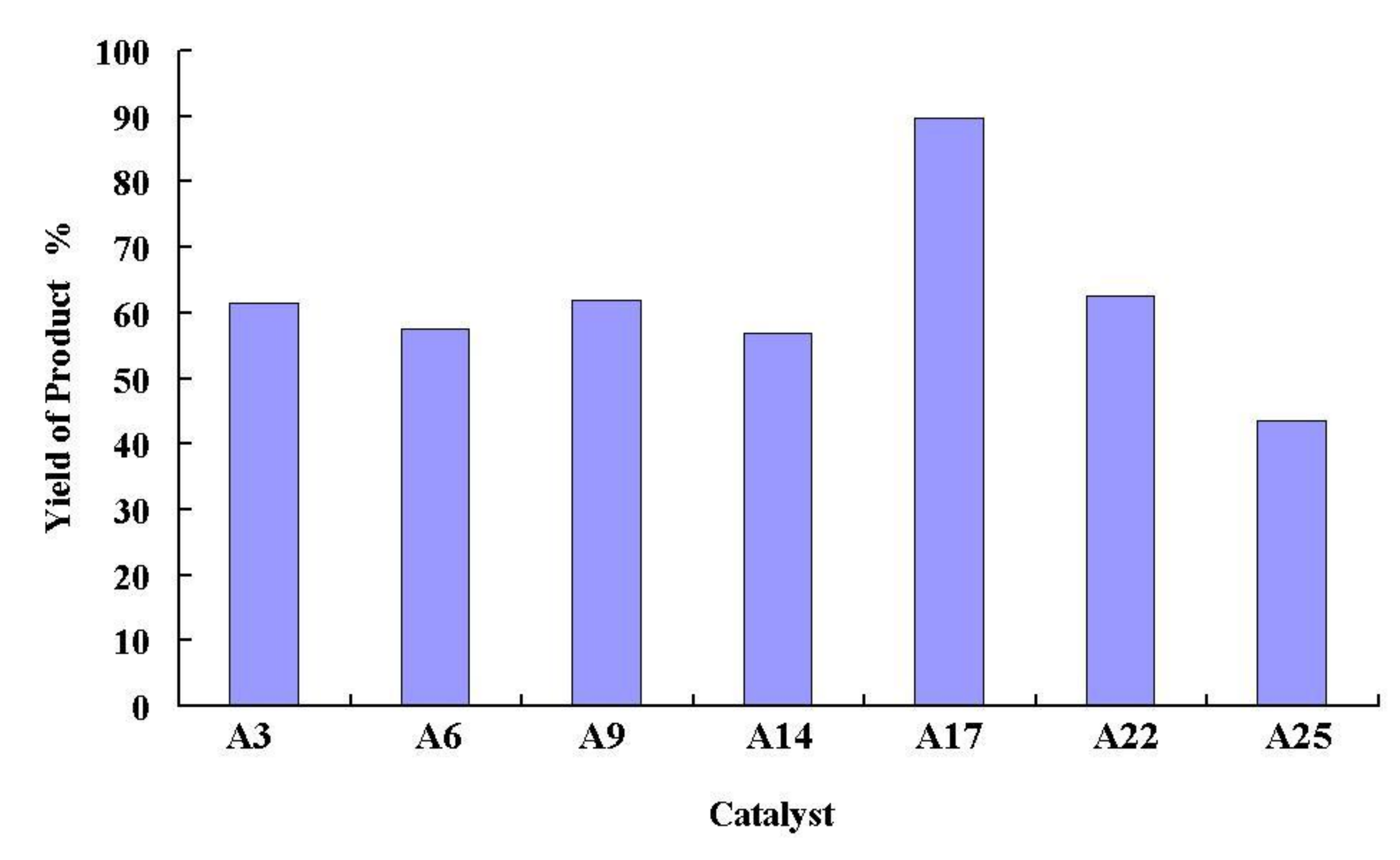
Catalyst: Ni-Mo/Al2O3
At 350 C, 1000 psi, 0.5-2 ml/min

Co-pyrolysis oil from Corn stover : tire = 1:1

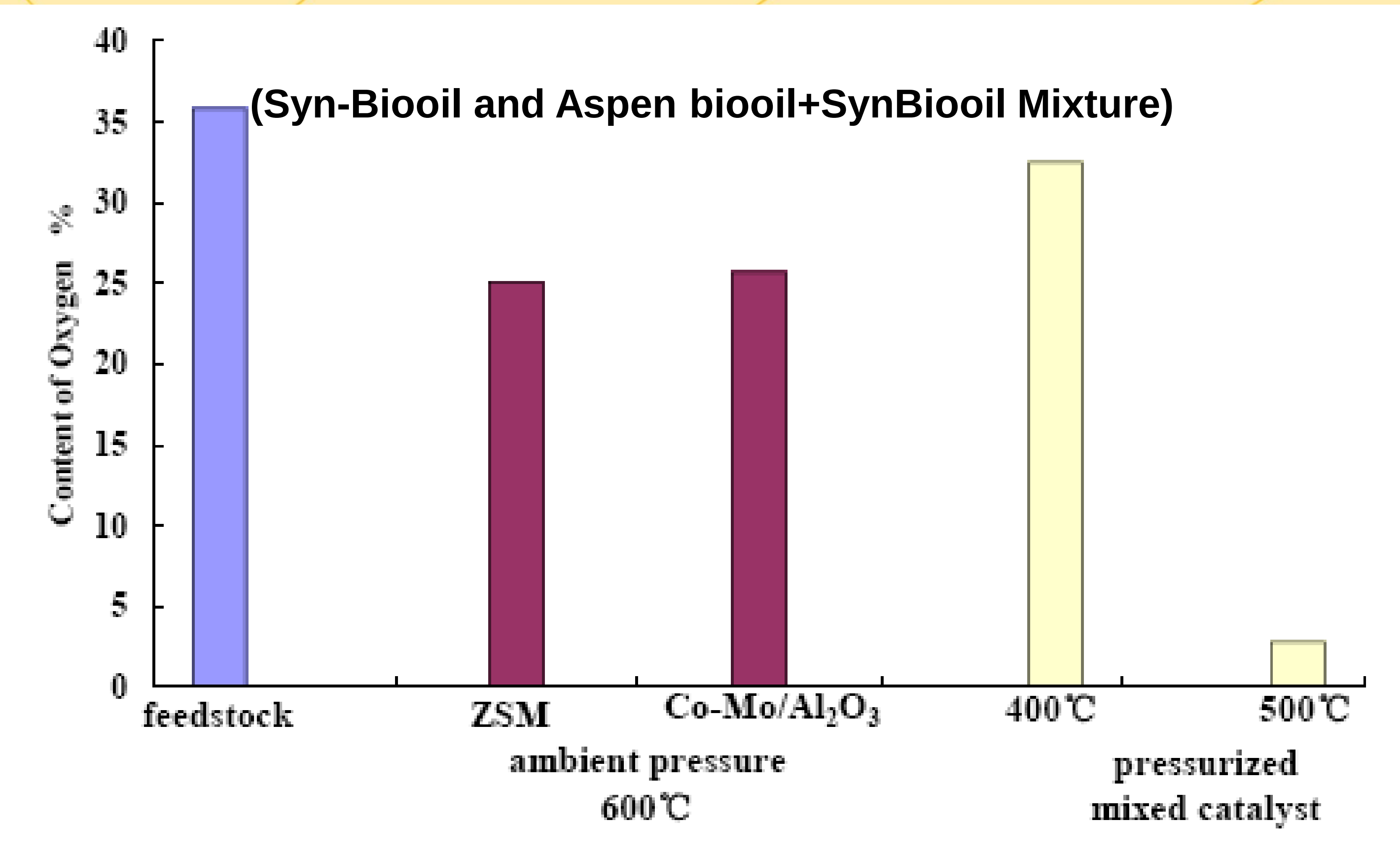
Oleic acid conversion over catalysts



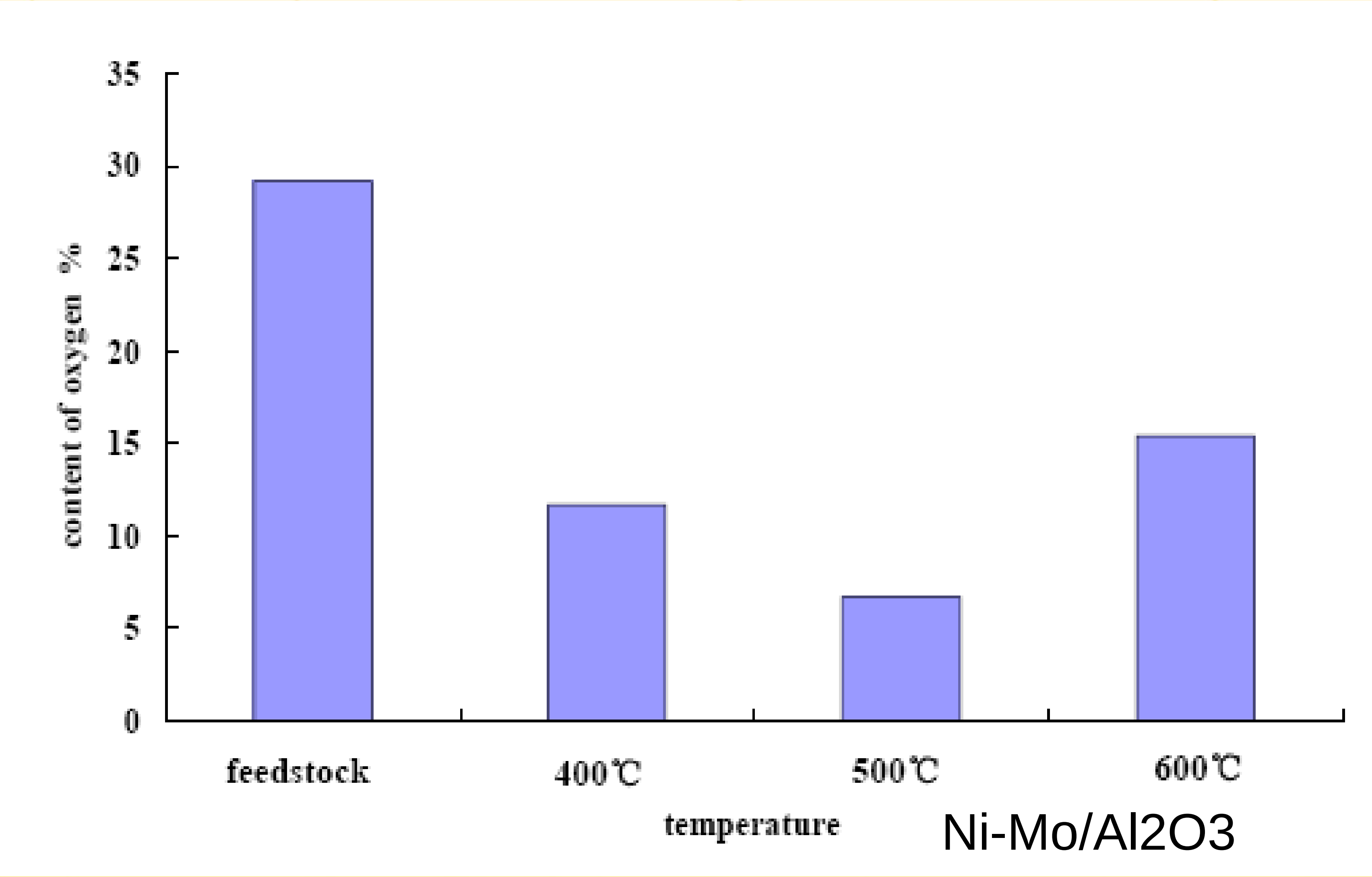
Liquid product yield of Canola oil over various catalysts



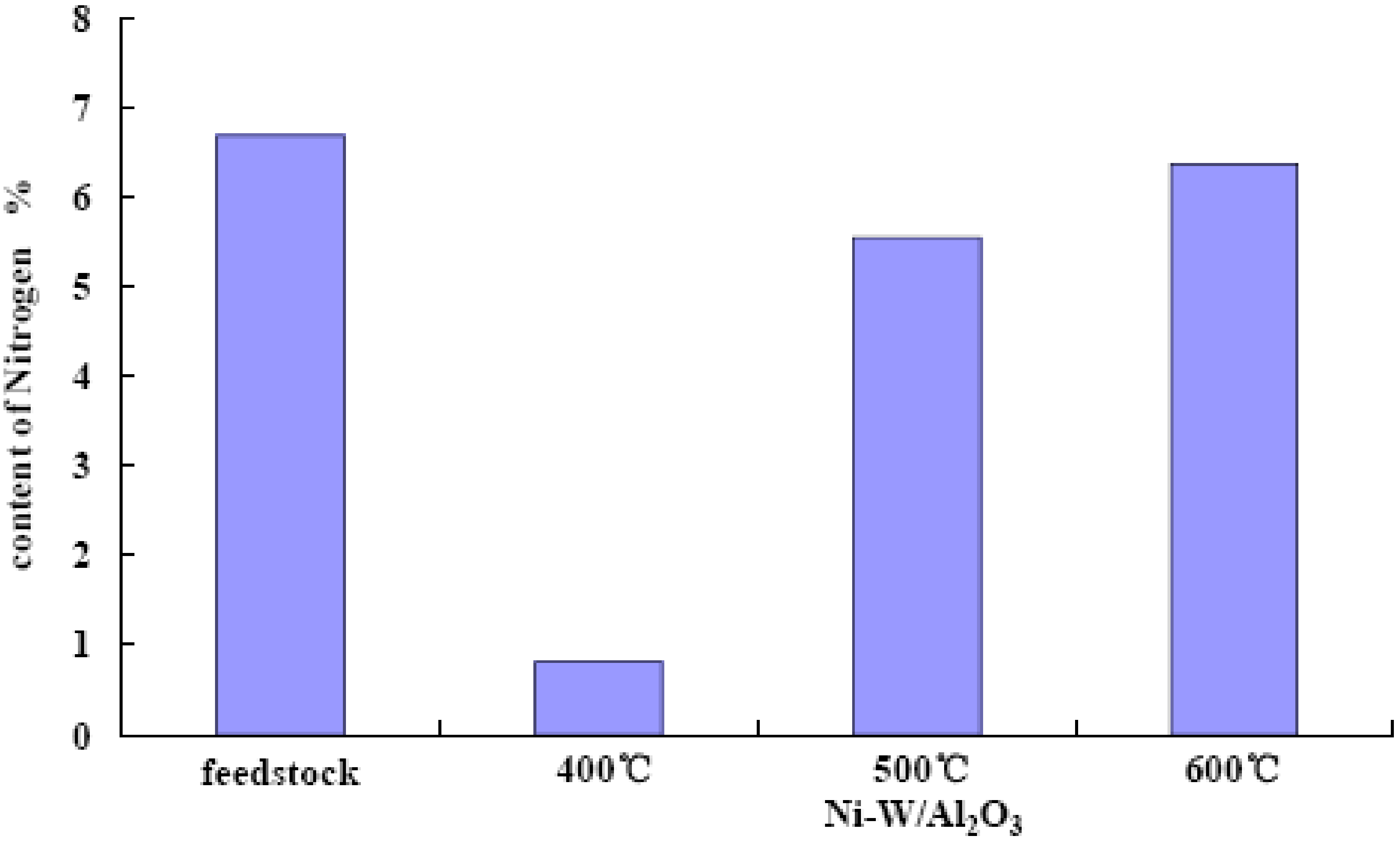
HydroDeOxygenation (HDO) of Model Compounds



HDO of N-O containing compound solution



HDN of N-O containing compound



Heating values (HHV, measured by bomb calorimeter, Cal/g)

High heating value of feedstocks

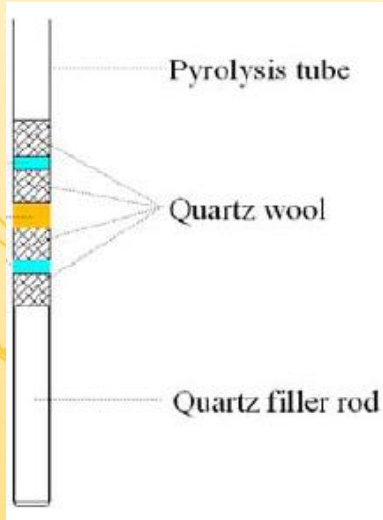
Oleic acid	Lineolic acid	Canola oil	JP-8	Gasoline
9446.5	9451.1	9310.2	10982.3	10794.6

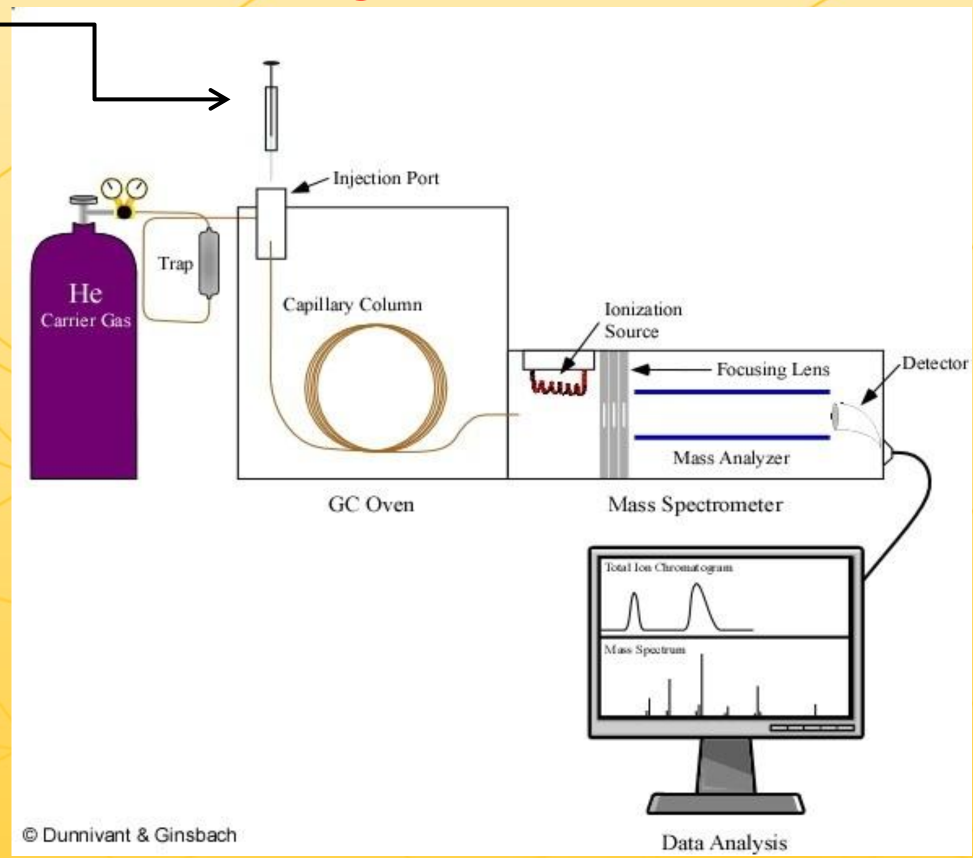
High heating value of products

A-6	A-7	A-8	A-23	A-27
9651.7	10023.6	9856.5	9554.0	9609.4

Note: The heating value of gasoline from internet, the other were measured in the lab

Pyrolyzer-GC/MS:
Quick and convenient catalyst screening method





Biomass (yellow) is pyrolyzed in the quartz tube and vapors go through the catalysts bed (blue) and then analyzed by GC/MS.

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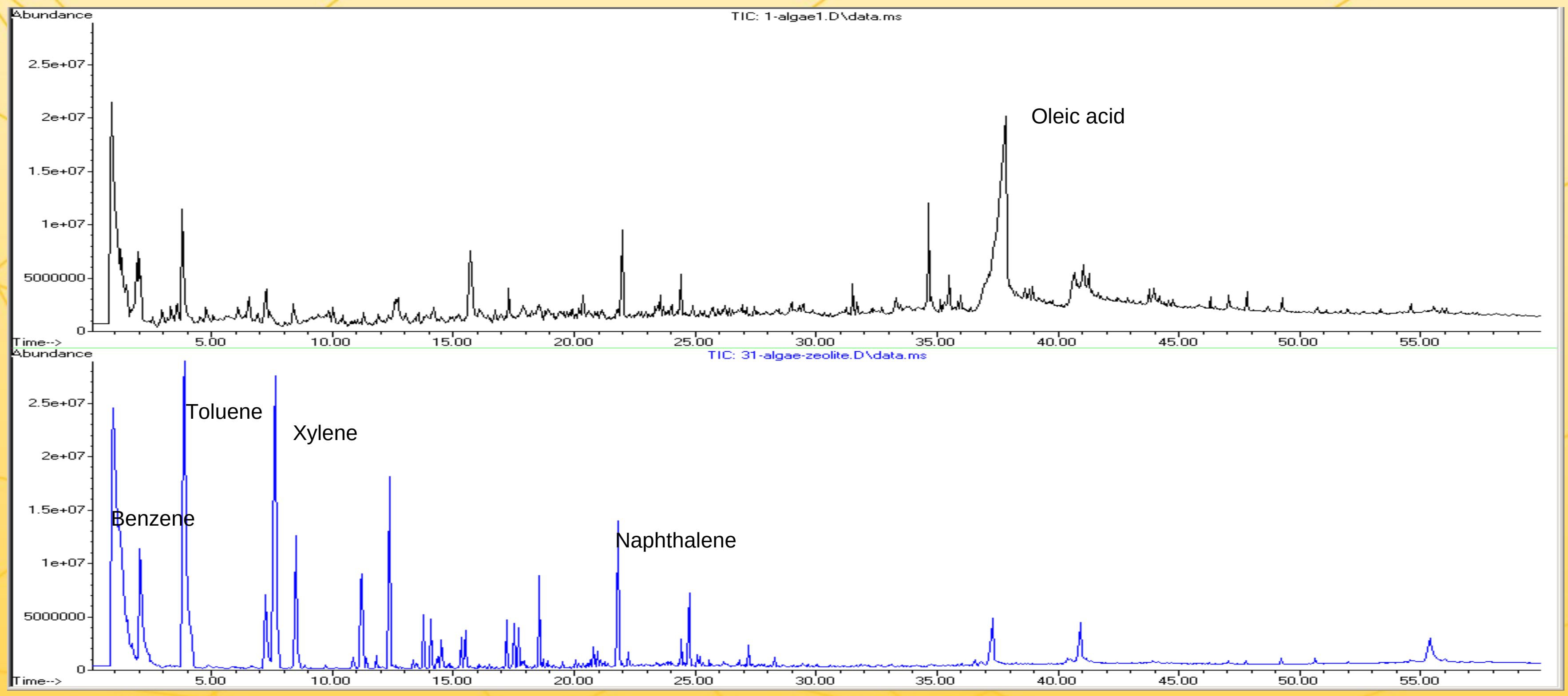
Microwave Assisted Catalytic Pyrolysis

Direct catalytic pyrolysis of algae



- Aromatic hydrocarbons are the major pyrolysis products (74% yield) with the use of catalyst A.
- Acetic acid, furfural, N-containing compounds and fatty acids were converted to aromatics.

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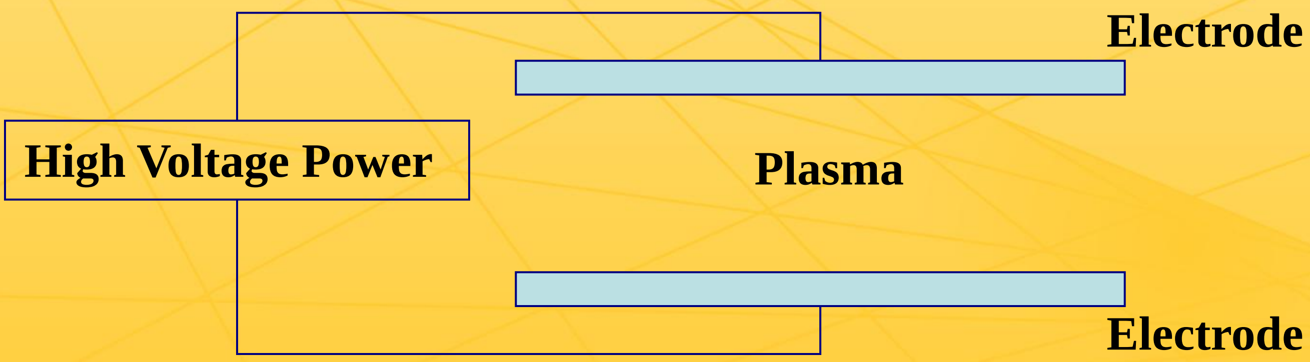
NTP-Assisted Catalytic Reforming

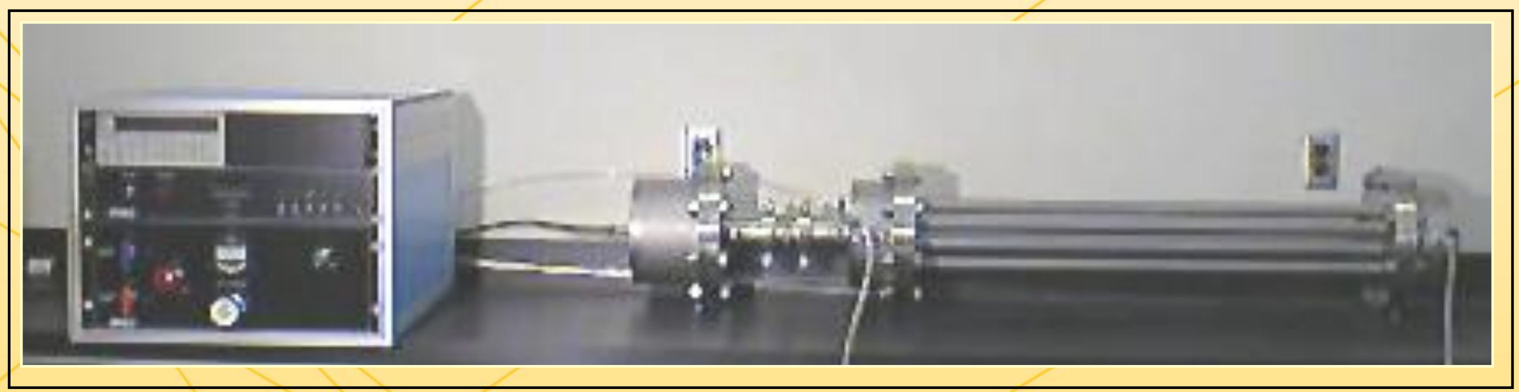
- Catalytic reforming has become a useful way to produce biofuels and other chemicals
- Conventional catalytic reforming usually requires high temperature and high pressure
- Catalysts can perform well at low temperature and pressure with assistance of Non-thermal Plasma (NTP).

NTP Reactor

Energetic electrons, ions, molecules, highly reactive radicals, etc. generated though electrical discharge in syngas to help synthesize liquid fuels and chemicals

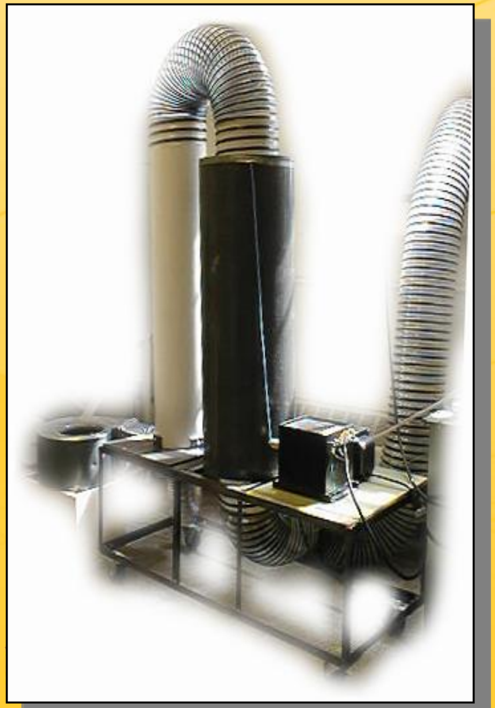


Pulsed Corona Discharge Reactors

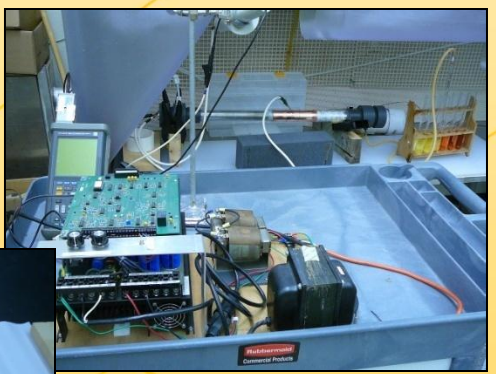
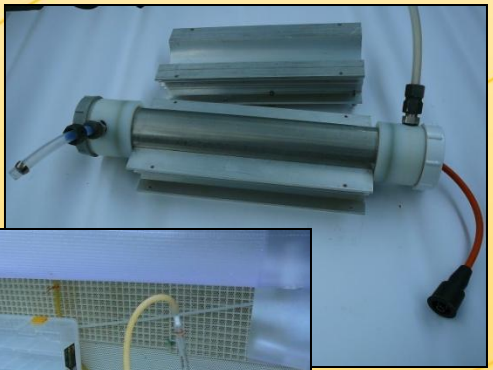
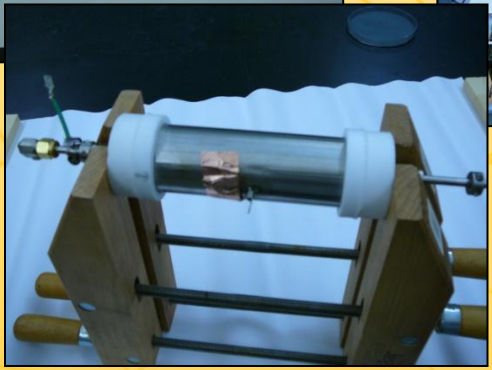


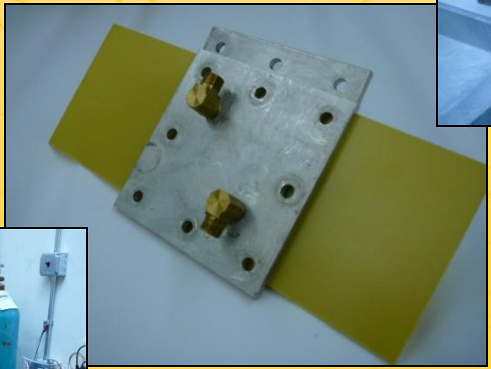
Silent discharge reactors

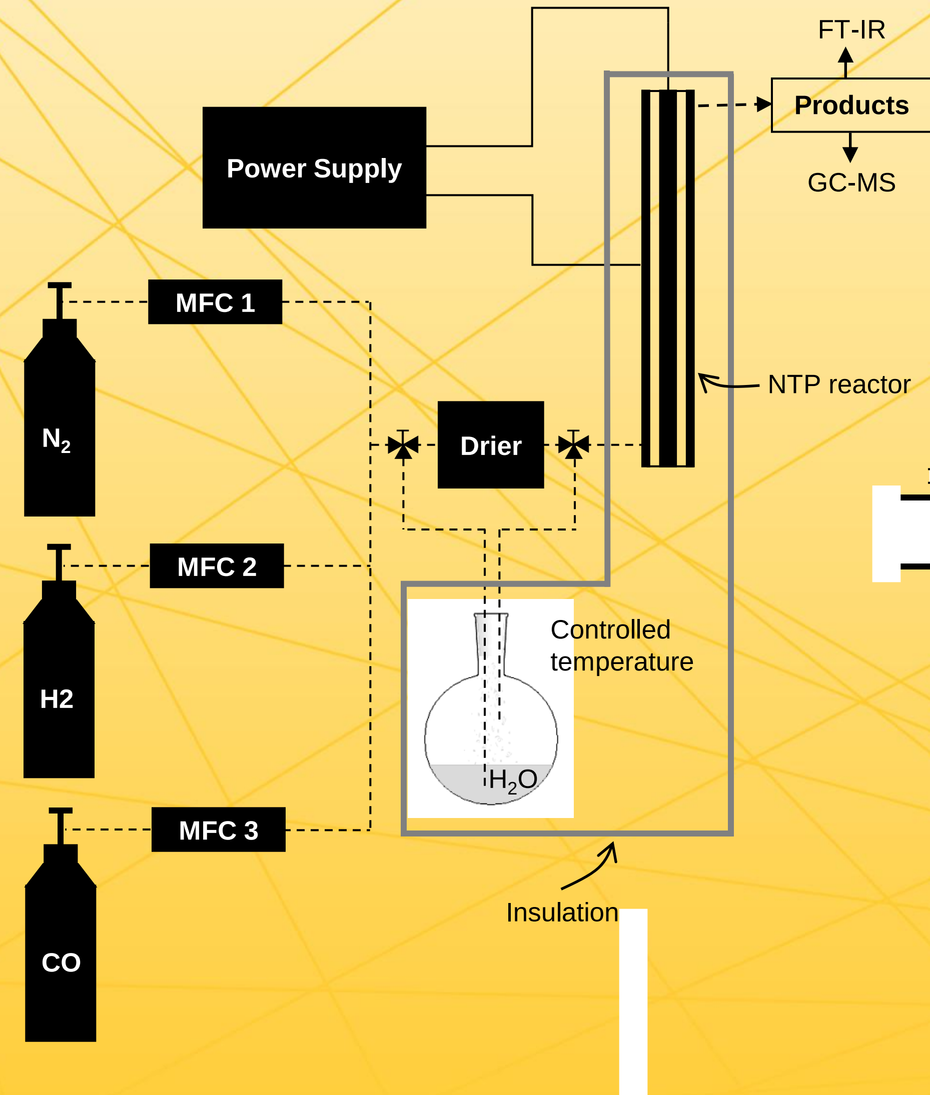
NTP Reactors

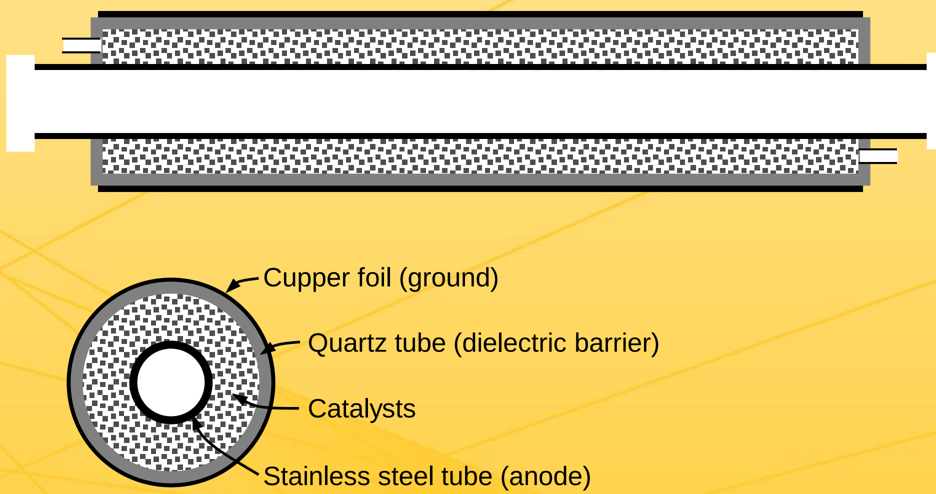


NTP Reactors for Catalytic Reforming







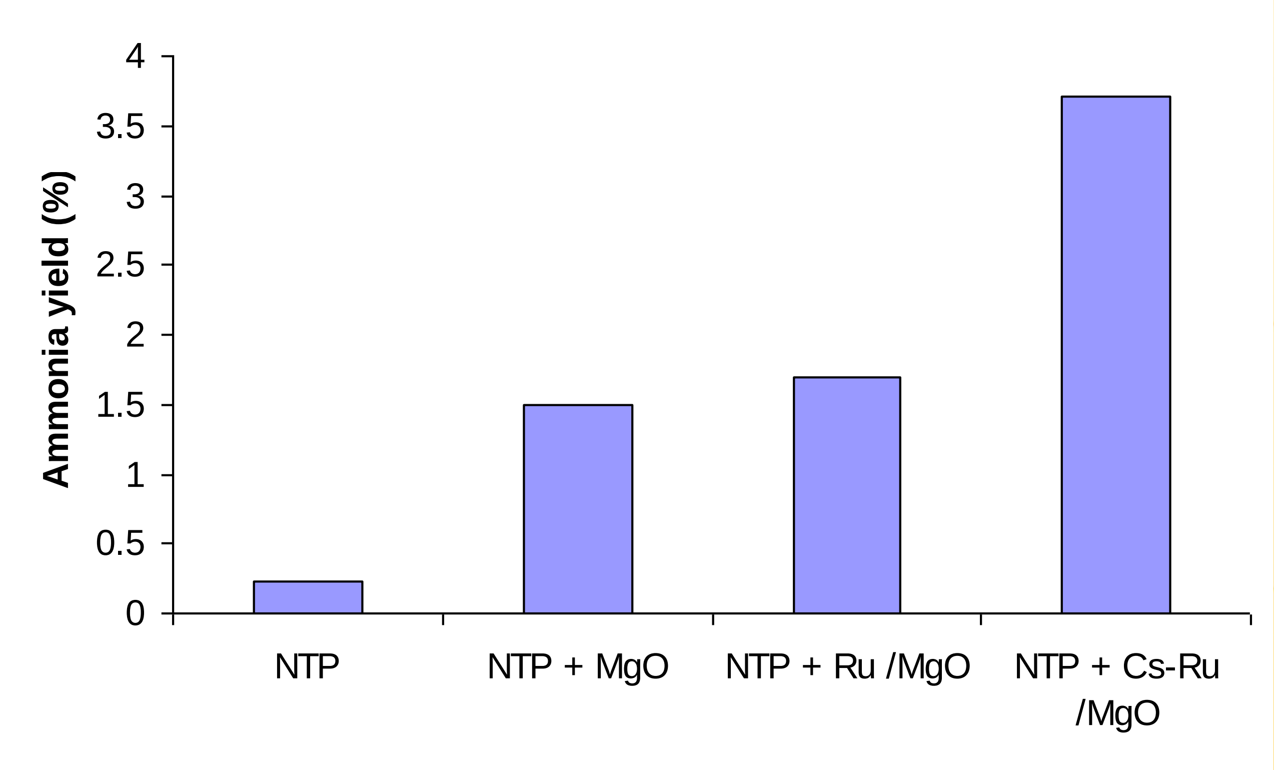
Cross section of the NTP reactor

Ionizations of Nitrogen and Hydrogen with NTP-Assisted Catalysis

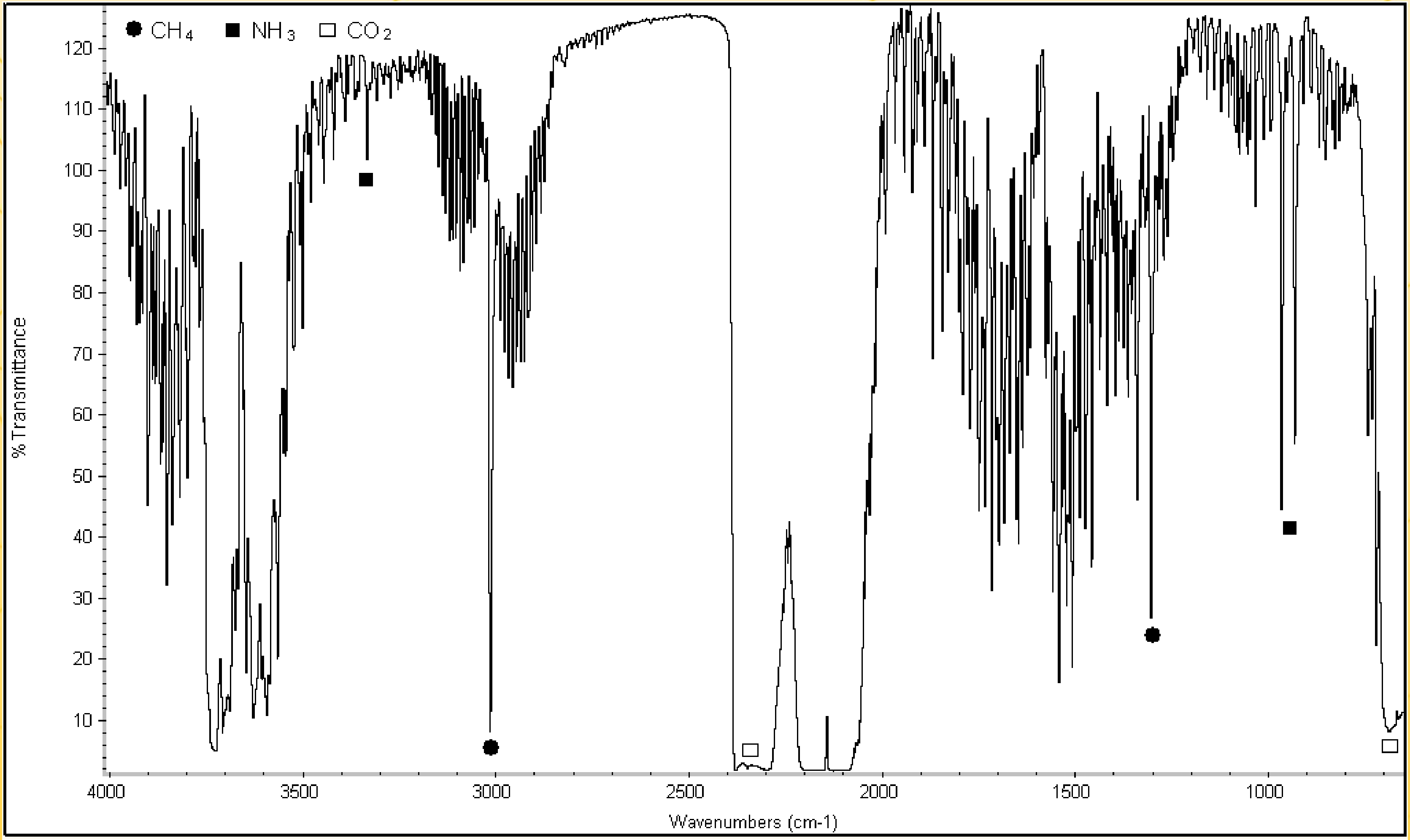
- $N_2 \rightarrow 2N^+$
- $H_2 \rightarrow 2H^+$
- $N^+ + H^+ \rightarrow NH^+$
- $NH^+ + H^+ \rightarrow NH^{2+}$
- $NH^{2+} + H^+ \rightarrow NH^{3+}$

Example - Ammonia Production

- 12% + ammonia produced at 150 °C and atmospheric pressure
- Potential to reach higher concentration with further optimization of catalysts and conditions
- Low capital, operation, and maintenance costs



NTP Ammonia synthesis different catalysts.
(V_{N2}:V_{H2}=1:3, N_2 and H_2 total flow rate 60ml/min, voltage 5000V, frequency 8000Hz.)



FT-IR spectrum of NTP reforming of N_2, CO, H_2 and/or H_2O vapor.

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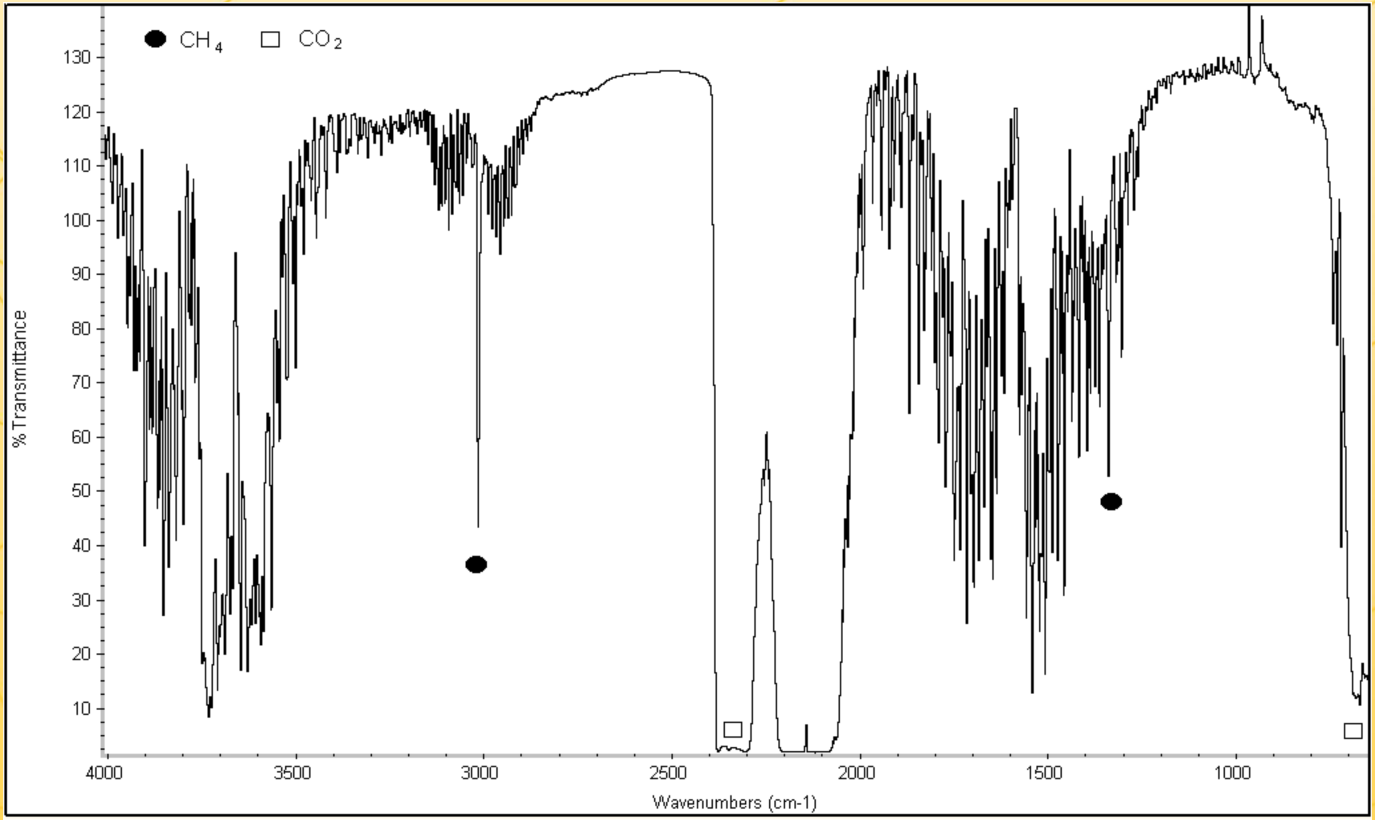
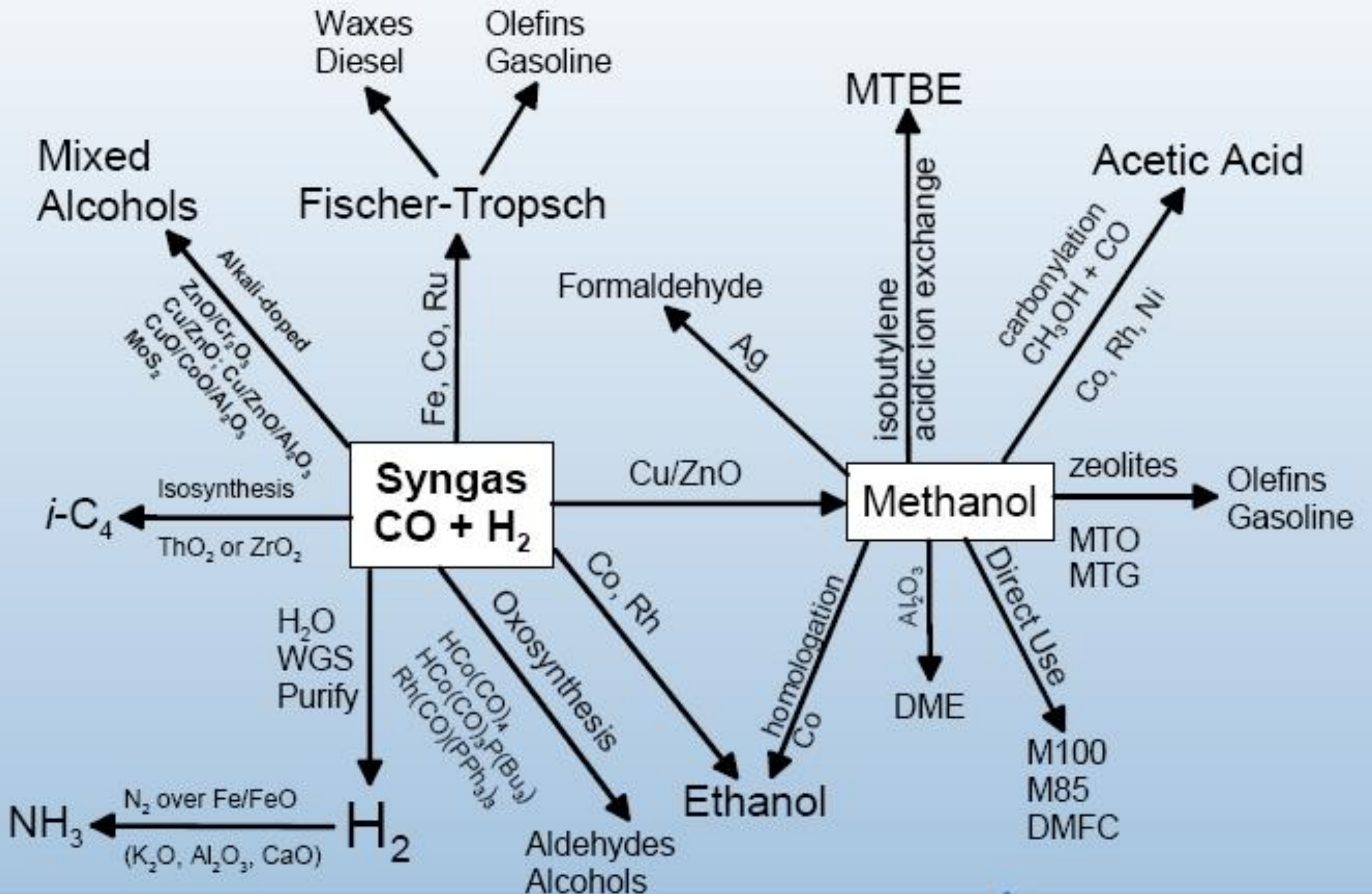


FT-IR spectroscopy of NTP reforming of CO and H_2O vapor.

Products from Syngas



NREL National Renewable Energy Laboratory

Summary

- The microwave-assisted catalytic pyrolysis technology has great potential for large scale demonstration and commercialization.
- The innovative NTP assisted catalytic reforming processes show many advantages over conventional high temperature and high pressures processes
- The pyrolysis time (i.e. retention time) plays an important role in oil quality and liquid product yield;
- Particle size is not a significant issue in terms of oil quality (composition) and product yield distribution;
- Co-pyrolysis of solid wastes such as scrap tires/plastics and biomass is practically feasible;
- With the aid of catalyst, the quality (heating value, O and N content, etc.) of the pyrolytic oil (bio-oil) can be significantly improved.

Center for BioRefining

Unlimited Possibilities

About the Center

The center is formed under the umbrella of IREE. Full Membership is open to the entire faculty of the University of Minnesota. Affiliate Membership is open to the biobased community outside the university.

Objectives

- To establish a network of multi-disciplinary researchers, state and federal government officials, and private-sector organizations and entities who share the same interest in development and use of biobased production technologies
- To identify opportunities in production and marketing of bioenergy and biomaterials
- To identify public and private funding sources Design and facilitate research programs
- To incorporate biobased production information in existing courses and curricula
- To create plan to educate the public and promote the use of bioenergy and biomaterials

- Research
- Technology Innovation
- Outreach & Education

BioEnergy

BioMaterials

BioChemicals

Bio-Economy

Sustainability

Http:// biorefining.cfans.umn.edu

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Questions?

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