Thermal Conversion Processes of Agro-industrial Wastes

3rd FOREBIOM Workshop

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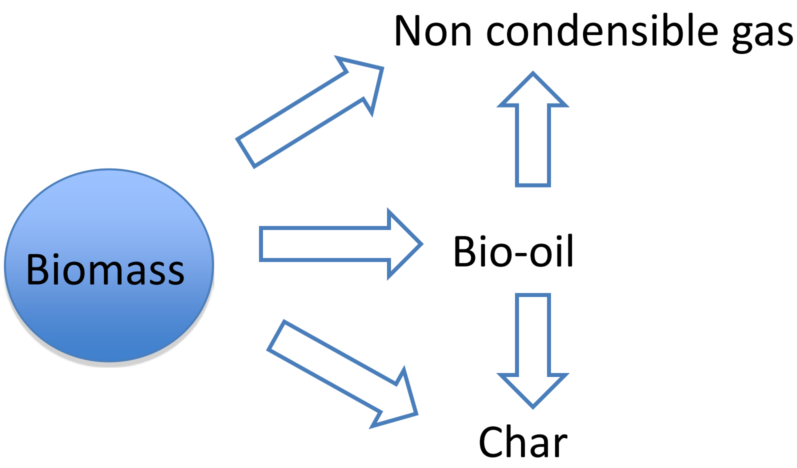
Concept of Presentation

- ✓Slow Pyrolysis of Agricultural Biomasses
- ✓Comparison of Fast and Slow Pyrolysis of Biomass
- ✓ Steam Reforming of Bio-oil

SLOW PYROLYSIS OF AGRICULTURAL BIOMASSES



	Conditions	yield, %		
		liquid	Char	Gas
Carbonisation	low temperature ,long residence time	30	35	35
Gasification	high temperature ,long residence time	5	10	85
Fast pyrolysis	moderate temperature, short residence time	75	12	13

SLOW PYROLYSIS OF AGRICULTURAL BIOMASSES

WHAT IS BIO-OIL?

- **Bio-oil consists of many oxygenated organic chemicals and is mostly water miscible.**

- dark brown liquid, combustible
- heating value ~ 17 MJ/kg, pH ~ 2.5
- pungent odour
- viscosity increases with time
- Comprised of numerous suspended chemical compounds (100 or more)

- **It can be stored and transported.**
- **It can be used as chemical feedstock.**

SLOW PYROLYSIS OF AGRICULTURAL BIOMASSES

Gas (COx, H_2, light hydrocarbons)

- can be used to heat pyrolysis reactor

Char

- Process heat
- Activated carbon
- Soil amendment

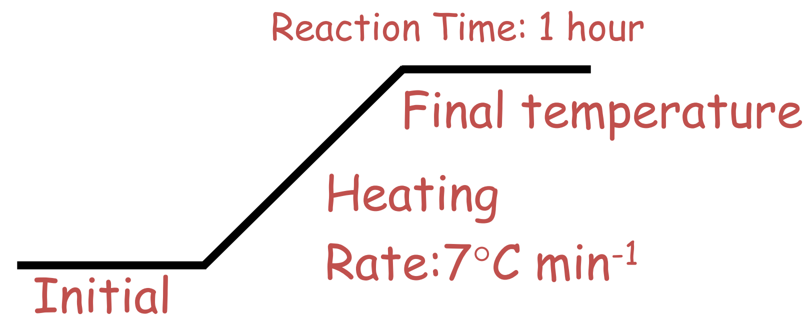
SLOW PYROLYSIS OF AGRICULTURAL BIOMASSES

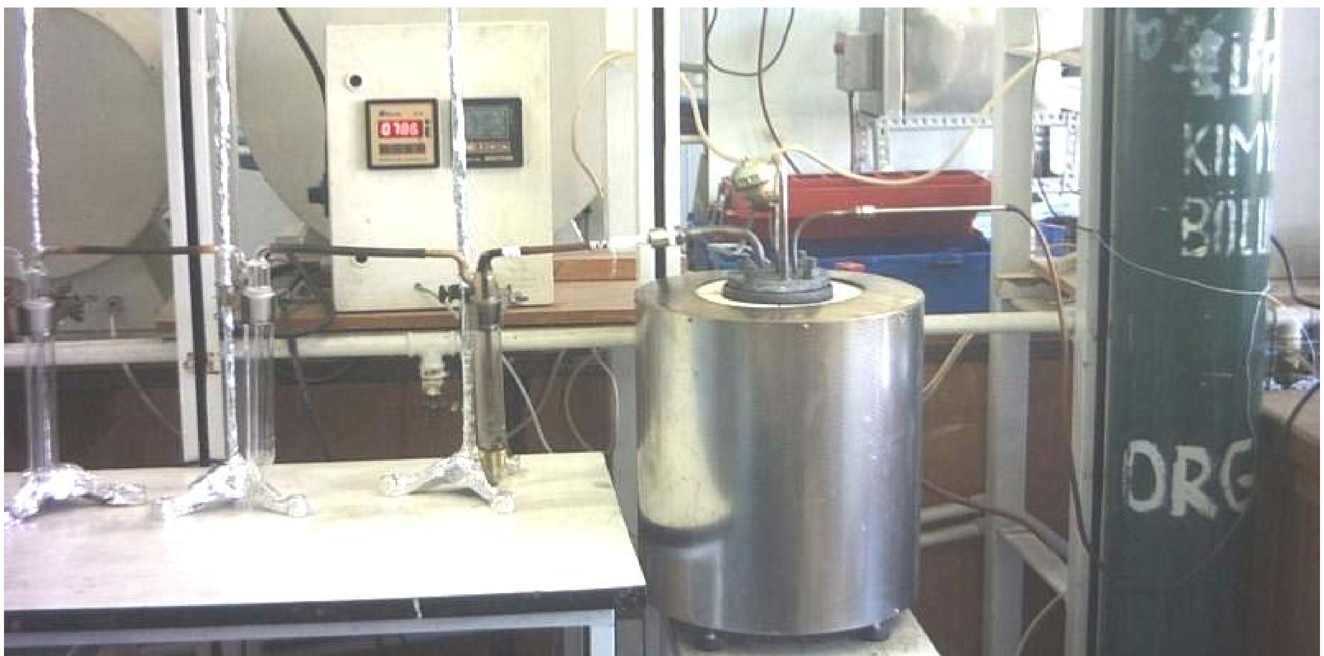
Experiments

Atmosphere: N_2

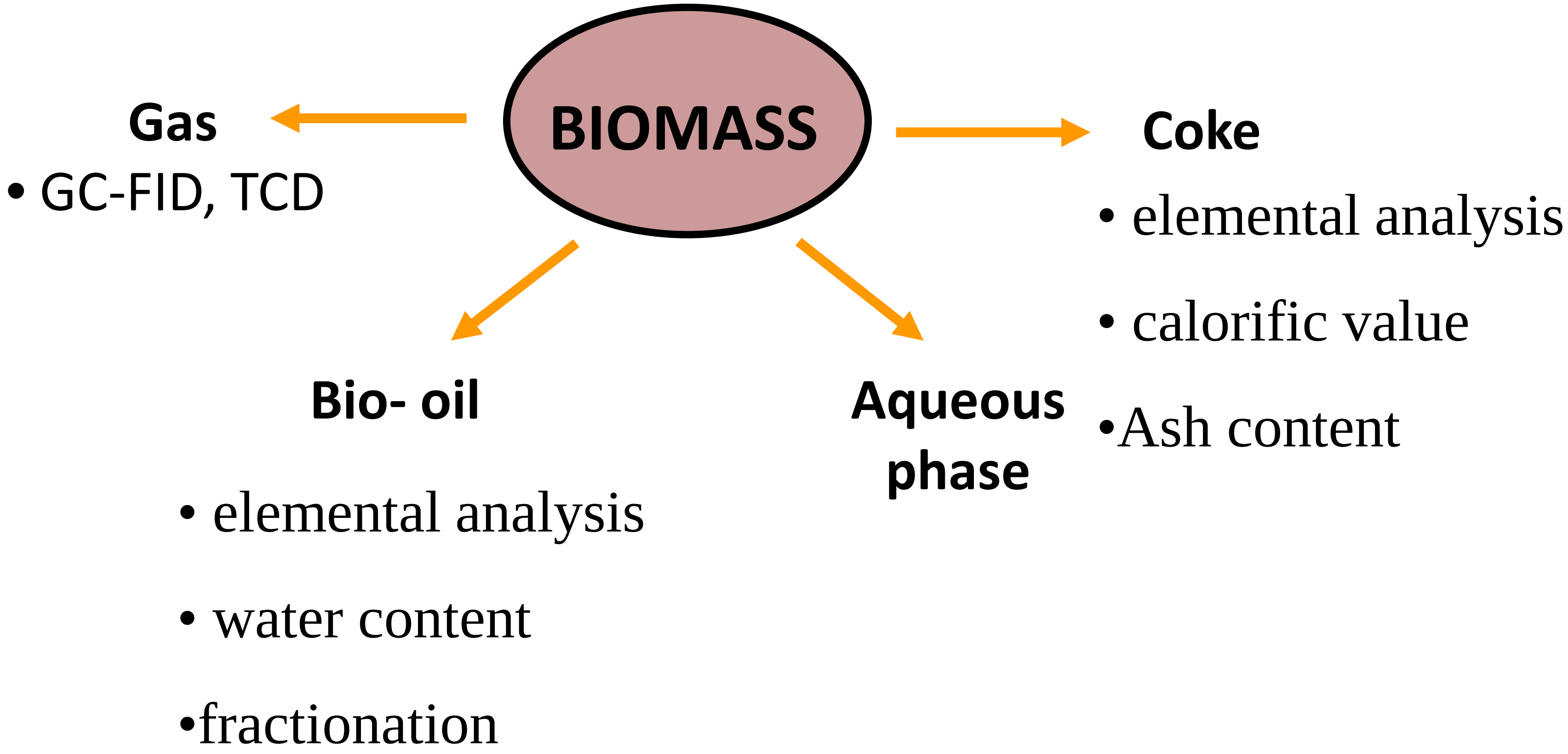
Flow Rate: 25 $cm^3 min^{-1}$

Sample Amount: 100 g

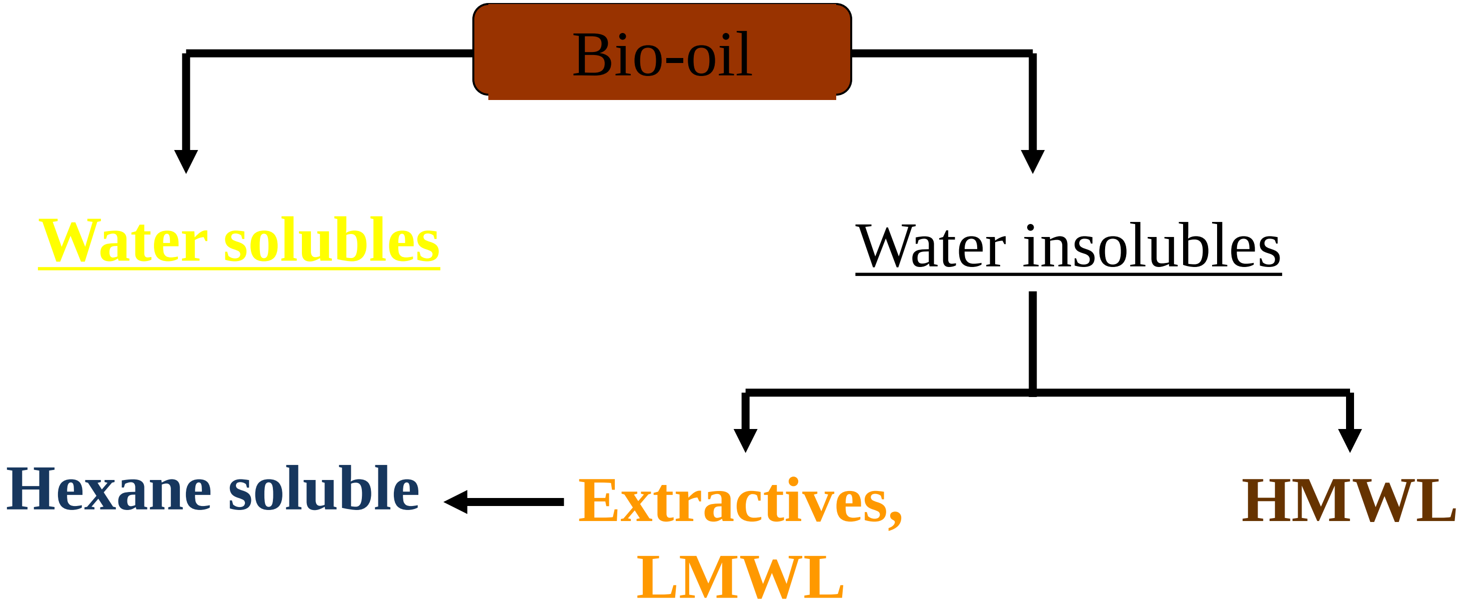




SLOW PYROLYSIS OF AGRICULTURAL BIOMASSES



Fractionation of Bio-oil*



*K. Sipila, E. Kuoppala, L. Fagernas, A. Oasmaa, Biomass Bioenergy 14 (1998) 103–113.

SLOW PYROLYSIS OF AGRICULTURAL BIOMASSES

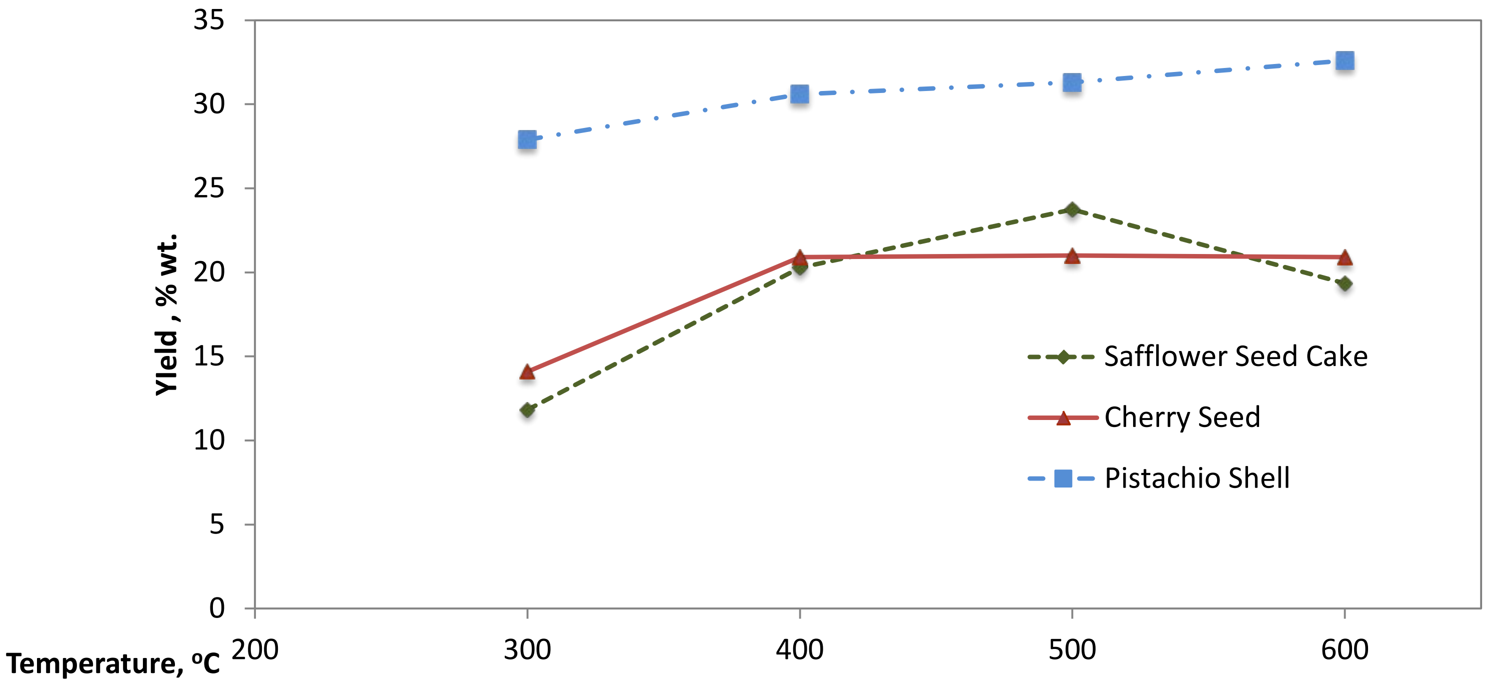
Results

Properties of Biomasses

	Safflower seed cake	Cherry Seed	Pistachio Shell
Proximate analysis (wt%)			
Moisture	6.9	5.5	7.0
Ash	3.8	1.2	0.9
Ultimate analysis (dry wt%)			
C	52.5	52.5	42.4
H	6.1	7.6	5.6
N	2.6	4.5	0.1
S	0.2	0.1	-
Component analysis (dry wt%)			
Cellulose	38.1	30.9	54.0
Lignin	12.3	29.1	25.3
Hemicellulose	39.5	28.6	20.1
Extractives	6.3	10.3	0.7

SLOW PYROLYSIS OF AGRICULTURAL BIOMASSES

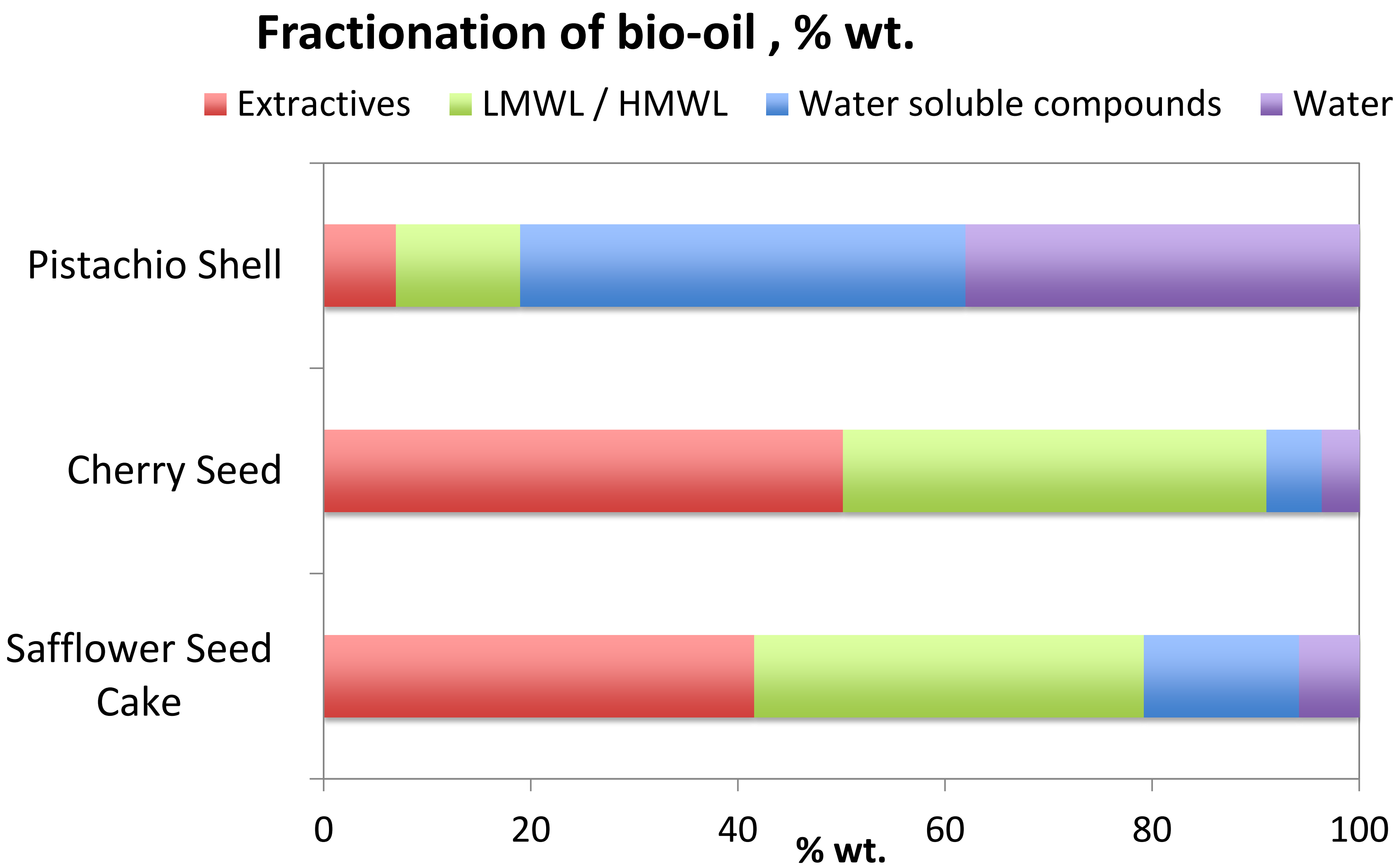
Bio-oil yield , % wt.



Char Yield, % wt.

	300	400	500	600
Safflower Seed Cake	44.2	35.2	30.8	30.8
Cherry Seed	39.6	29.9	26.2	24.9
Pistachio Shell	29.8	25.1	24.6	23.2

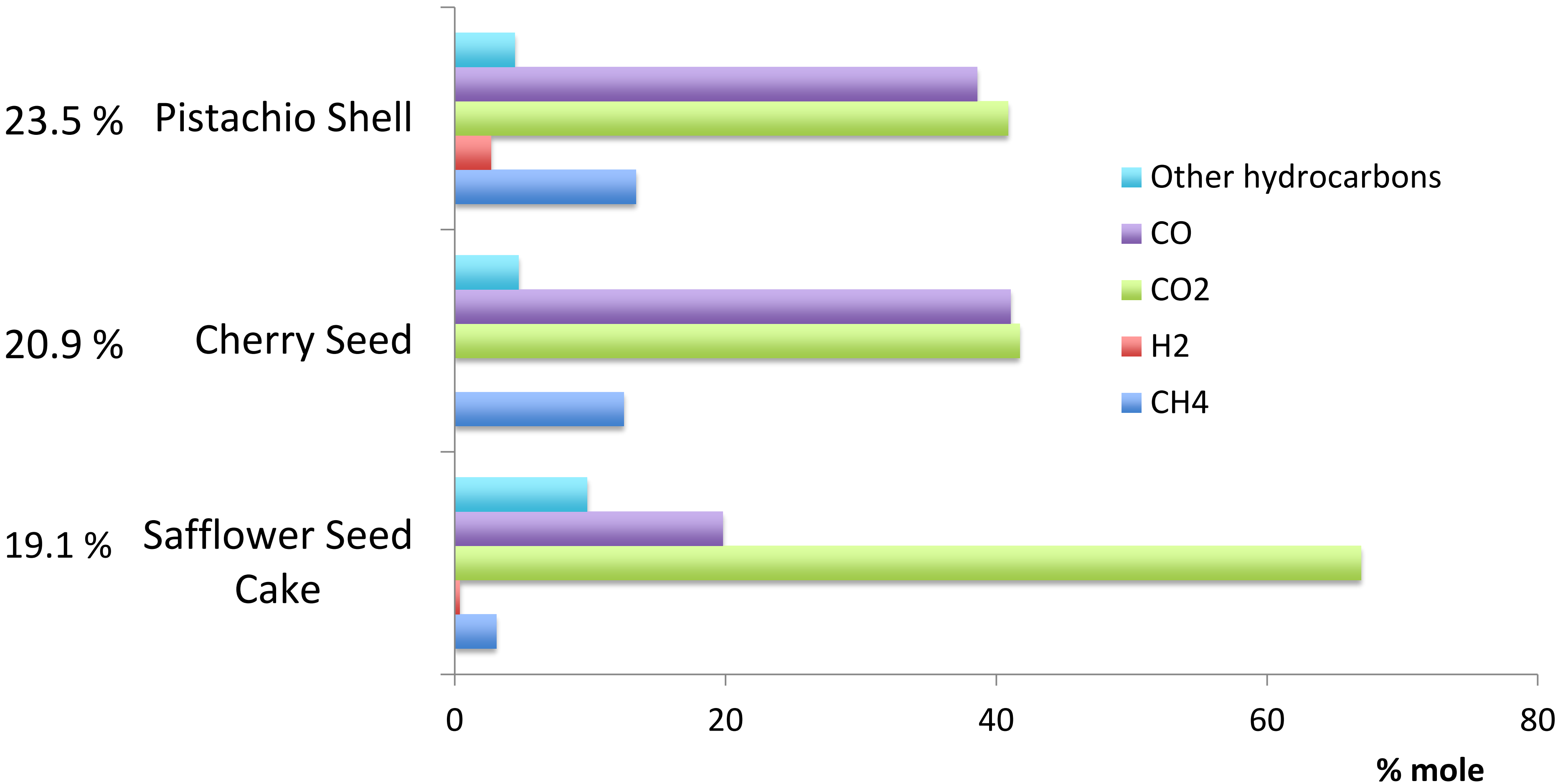
SLOW PYROLYSIS OF AGRICULTURAL BIOMASSES



*Obtained from 500 °C

SLOW PYROLYSIS OF AGRICULTURAL BIOMASSES

Gas Yield*, % wt. **Gas Composition, % mole**



*Calculated from difference

SLOW PYROLYSIS OF AGRICULTURAL BIOMASSES

Fuel Characteristic of Bio-oil

	Safflower seed cake	Cherry Seed	Pistachio Shell
Water Content, % wt.	5.8	5.6	38.4
Ultimate analysis (dry wt%)			
C	62.7	67.2	36.6
O	25.8	21.9	53.3
H	7.7	8.5	7.2
N	3.7	2.5	2.8
S	0.1	-	0.1
Calorific value, MJ/kg	28.3	32.5	13.6

Properties of chars

	Pistachio Shell	Cherry Seed	Safflower Seed Cake
Elementel analysis, %wt.			
C	82.4	77.8	69.5
H	3.1	3.0	2.7
N	0.2	1.9	3.9
S	0.1	-	-
O	14.2	17.3	13.3
Ash content	0.6	3.4	10.6
HHV (MJkg-1)	29.7	31.1	25.8

SLOW PYROLYSIS OF AGRICULTURAL BIOMASSES

- Cherry seed is feasible biomass for producing bio oil in terms of fuel characteristic.
- Although pistachio shell gave the highest yield of bio-oil, it had a low fuel quality relating to its high water content.
- Bio-oil from pistachio shell can be used as a source of chemicals.

SLOW PYROLYSIS OF AGRICULTURAL BIOMASSES

Antifungal activity of biooil derived Pistachio shell

			Inhibition, %
•*Aspergillus niger* TEM	➔	a saprophytic fungus	**17.4-65.2**
•*Trichoderma viridae* TEM	➔	a phytopathogenic fungus	**21.7-69.5**
• *Coriolus versicolor* ATCC 200801	➔	a white rot fungus	**30.4-82.6**
•*Trichophyton rubrum*	➔	a dermatophytic fungus	**47.8-95.6**

incubated at 27 ºC for 10 days

SDA plates were prepared and then three holes were punched in periphery and a forth at the centre

+

50 µl of diluted bio-oil with %1 dimethylsulfoxide

(2-10-20-30-40-50 mg bio-oil ml^{-1})

Distance between peripheral holes and the rim of the fungal colony were measured after 10 days.

COMPARISON OF SLOW AND FAST PYROLYSIS

Biomass: Cherry seed

Pyrolysis Experiments

Fixed bed Reactor

Temperature
- 300ºC
- 400ºC
- 500ºC
- 600ºC

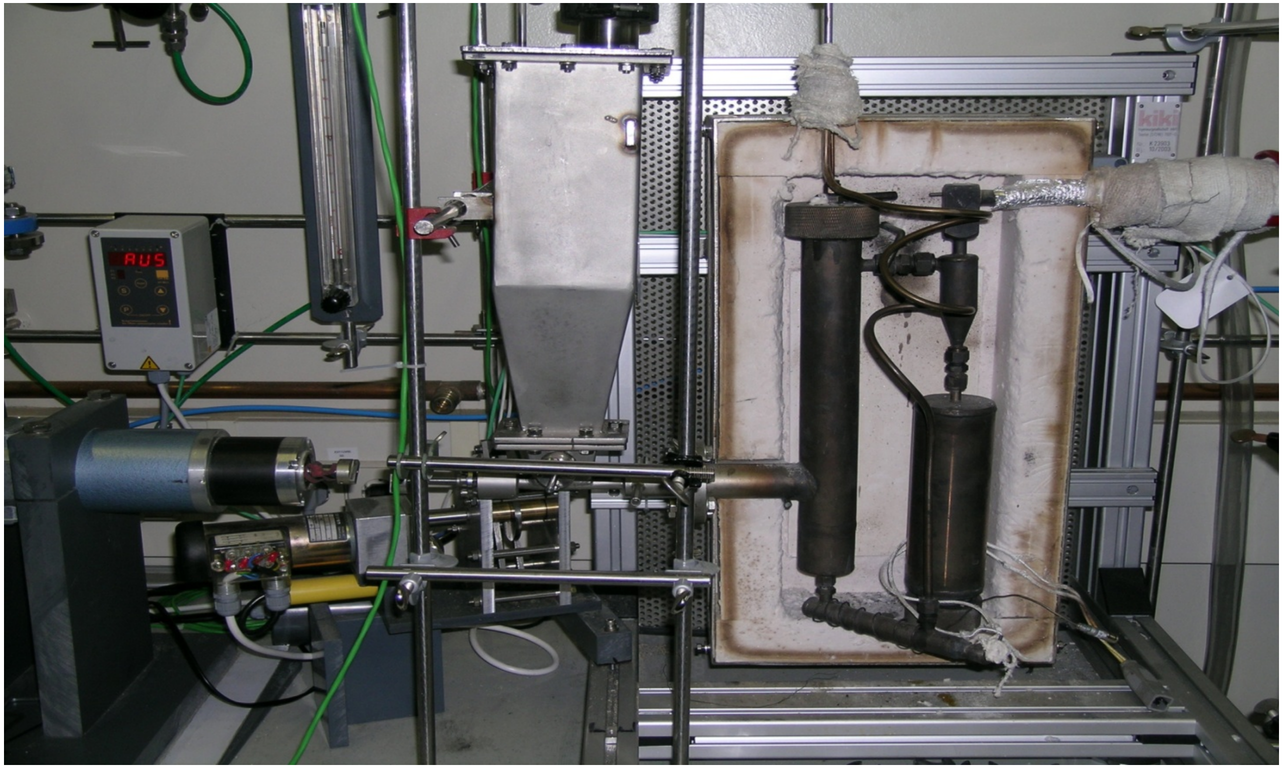
Fluidized bed Reactor

Temperature
- 400ºC
- 500ºC
- 600ºC

COMPARISON OF SLOW AND FAST PYROLYSIS

Experiments

FLUIDIZED BED REACTOR(ID: 40 MM, LENGTH 300 MM)



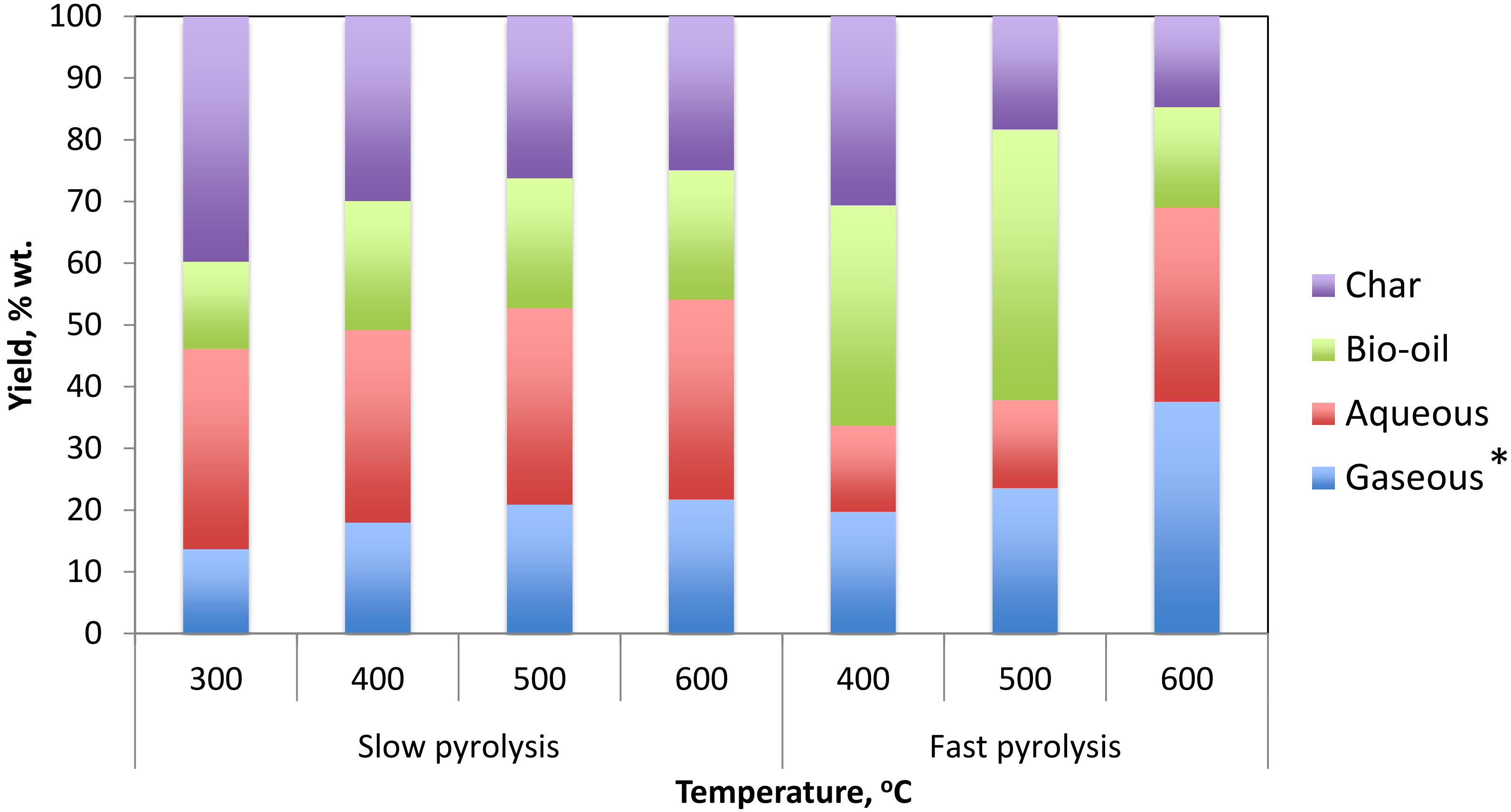
Silica sand (450 µm) with a static bed depth of 37 mm

Gas velocities: 0.25-0.30 m/s   Residence time of gas: 1-2 s

Feed: 100- 120 g

COMPARISON OF SLOW AND FAST PYROLYSIS

Results



* calculated from mass balance

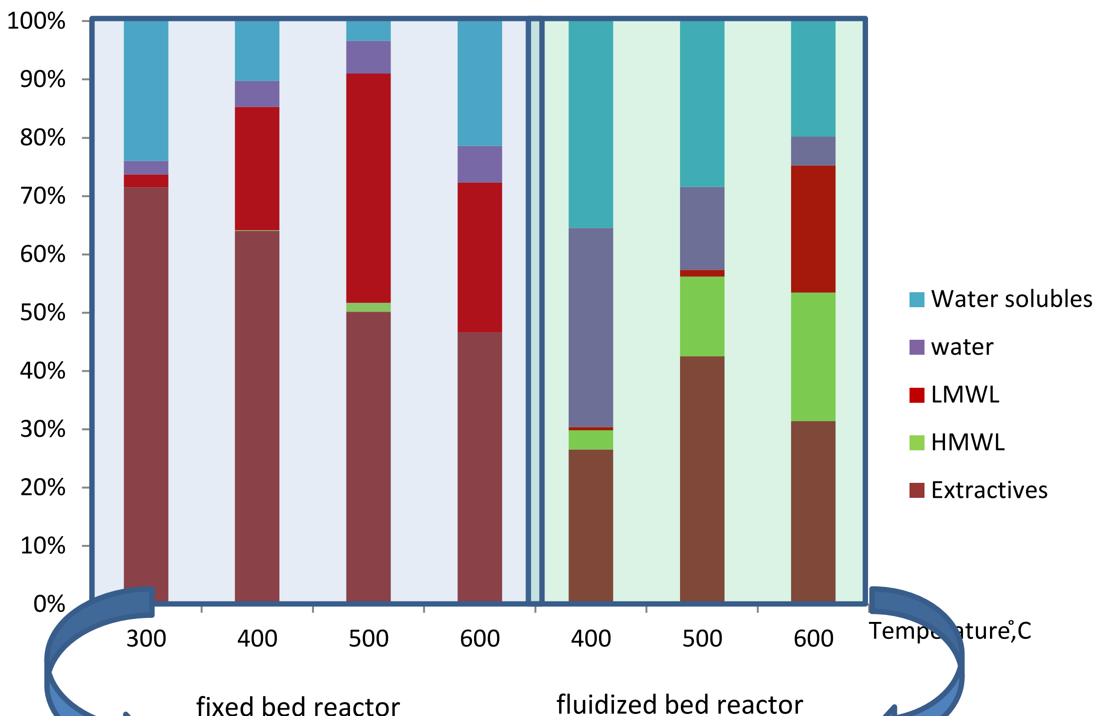
COMPARISON OF SLOW AND FAST PYROLYSIS

Fuel Characteristic of Bio-oil

	Slow pyrolysis			Fast pyrolysis		
	400	500	600	400	500	600
Water content, % wt.	4.4	5.6	6.3	34.2	14.0	4.9
Ultimate analysis						
C	67.6	67.2	66.6	42.7	44.2	58.7
H	8.6	8.5	8.7	7.4	7.4	8.2
N	2.7	2.5	2.8	2.5	3.3	3.0
S	-	-	-	-	-	-
O	21.07	21.9	21.9	47.4	45.1	30.0
GCV MJ kg-1	32.0	32.5	31.0	23.1	24.2	24.5

COMPARISON OF SLOW AND FAST PYROLYSIS

Fractionation bio-oil phase



Degradation of cellulose and hemicellulose

↓

Water and water soluble

T ↑ Lignin degradation

↓

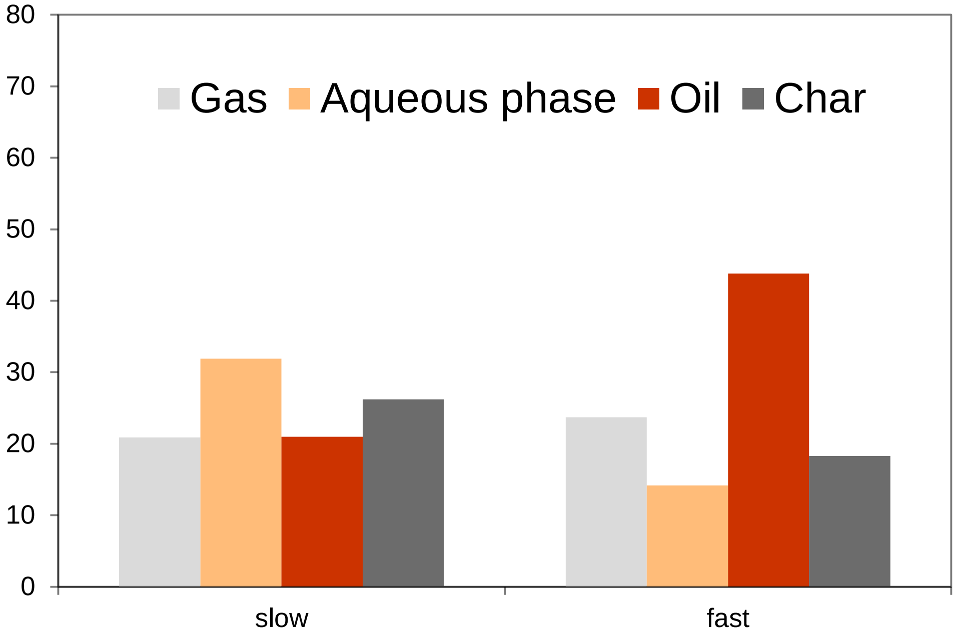
Pyrolytic lignin

Pyrolytic lignin → water soluble T ↑

T ↑ EXTRACTIVES ↓

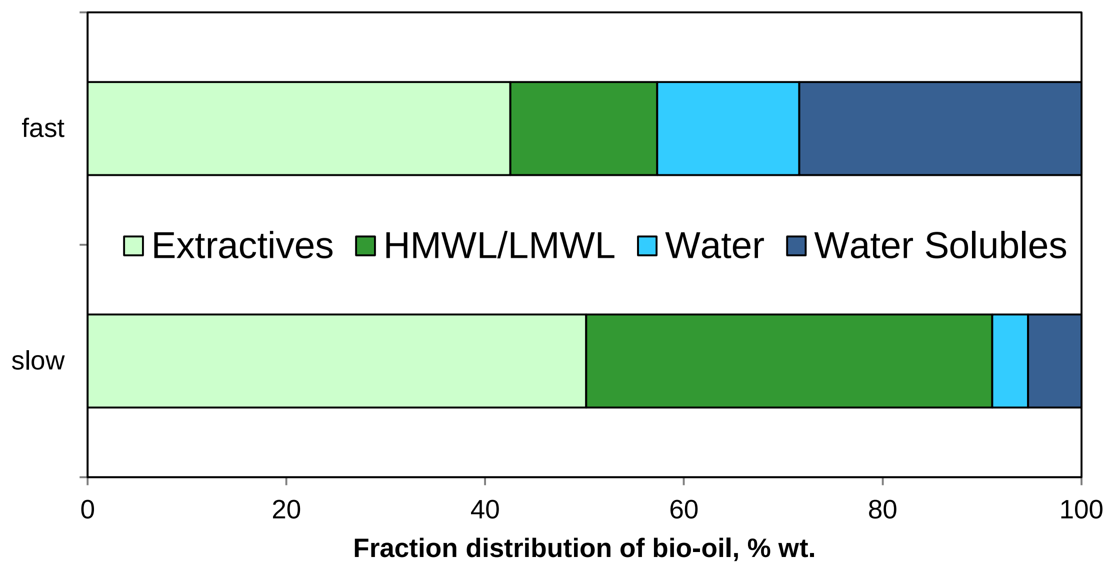
WATER AND WATER SOLUBLE ↓

COMPARISON OF SLOW AND FAST PYROLYSIS



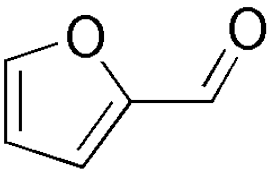
Characteristic of Bio-oil

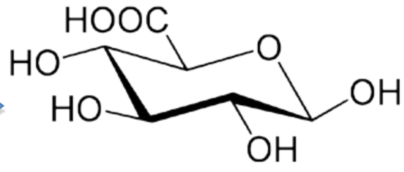
	slow	fast
Water content ,%	5.60	14.27
GCV*, MJ kg^{-1}	32.46	24.24
Ultimate Analysis ,%wt		
C	67.18	44.23
H	8.48	7.42
N	2.45	3.26
S	0.03	0.04
O	21.86	45.05

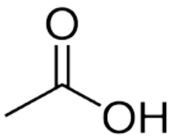


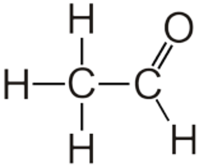
COMPARISON OF SLOW AND FAST PYROLYSIS

	Slow Pyrolysis at 500 ^oC	Fast Pyrolysis at 600 ^oC
Compounds, mg/g bio-oil		
Hydroxymethylfural	-	0.4
Furfural	0.1	2.1
Methylfurfural	-	0.2
Glycuronic acid	0.7	5.2
Formic acid	0.4	1.8
Acedic acid	26.4	5.6
Formaldehyde	-	1.0
Acetaldehyde	-	18.5
Total phenols	125	103









COMPARISON OF SLOW AND FAST PYROLYSIS

Slow pyrolysis	Fast pyrolysis
High yield of char product	Low yield of char product
Low yield of liquid product	High yield of liquid product
Low water content in oil	High water content in oil
Oil with higher calorific value	Oil with lower calorific value
Char can be used for producing activated carbon and heating	Char can be used only for heating

COMPARISON OF SLOW AND FAST PYROLYSIS

- The bio-oils from slow pyrolysis can be used as fuels for cumbustion systems in industry. But it is clear that they should be upgraded to receive an improved bio-oil composition for the direct utilization as a transport fuel.

- The bio-oil from fast pyrolysis having high water content and low calorific value can be considered as a chemical feedstock for valuable chemicals.

STEAM REFORMING OF BIO-OIL

≥700 °C

Steam-Tar reforming	$C_xH_y + 2x\ H_2O \rightarrow (2x+y)H_2 + xCO_2$
Water-gas Shift Reaction	$CO + H_2O \rightarrow CO_2 + H_2$

Metal based catalyts such as
Fe, Ni,Mg, Mn, Ce, Pt, etc.

↓

Coke deposition

STEAM REFORMING OF BIO-OIL

I&EC research
Industrial & Engineering Chemistry Research
Article
pubs.acs.org/IECR

Catalyst Properties and Catalytic Performance of Char from Biomass Gasification

Naomi B. Klinghoffer,[†] Marco J. Castaldi,[†,*] and Ange Nzihou[‡]

Energy Fuels **2010**, *24*, 76–83 · DOI:10.1021/ef9005109
Published on Web 08/14/2009
energy&fuels article

In-Situ Reforming of Tar from the Rapid Pyrolysis of a Brown Coal over Char[†]

Toru Matsuhara,[‡] Sou Hosokai,[‡] Koyo Norinaga,[§] Koichi Matsuoka,[‖] Chun-Zhu Li,[⊥] and Jun-ichiro Hayashi*,[‡]

Fuel 112 (2013) 646–653
Contents lists available at SciVerse ScienceDirect
Fuel
journal homepage: www.elsevier.com/locate/fuel
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FUEL

An advanced biomass gasification technology with integrated catalytic hot gas cleaning. Part II: Tar reforming using char as a catalyst or as a catalyst support

CrossMark

Shu Zhang[1], Mohammad Asadullah[2], Li Dong, Hui-Ling Tay, Chun-Zhu Li *

Applied Energy 88 (2011) 1656–1663
Contents lists available at ScienceDirect
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journal homepage: www.elsevier.com/locate/apenergy
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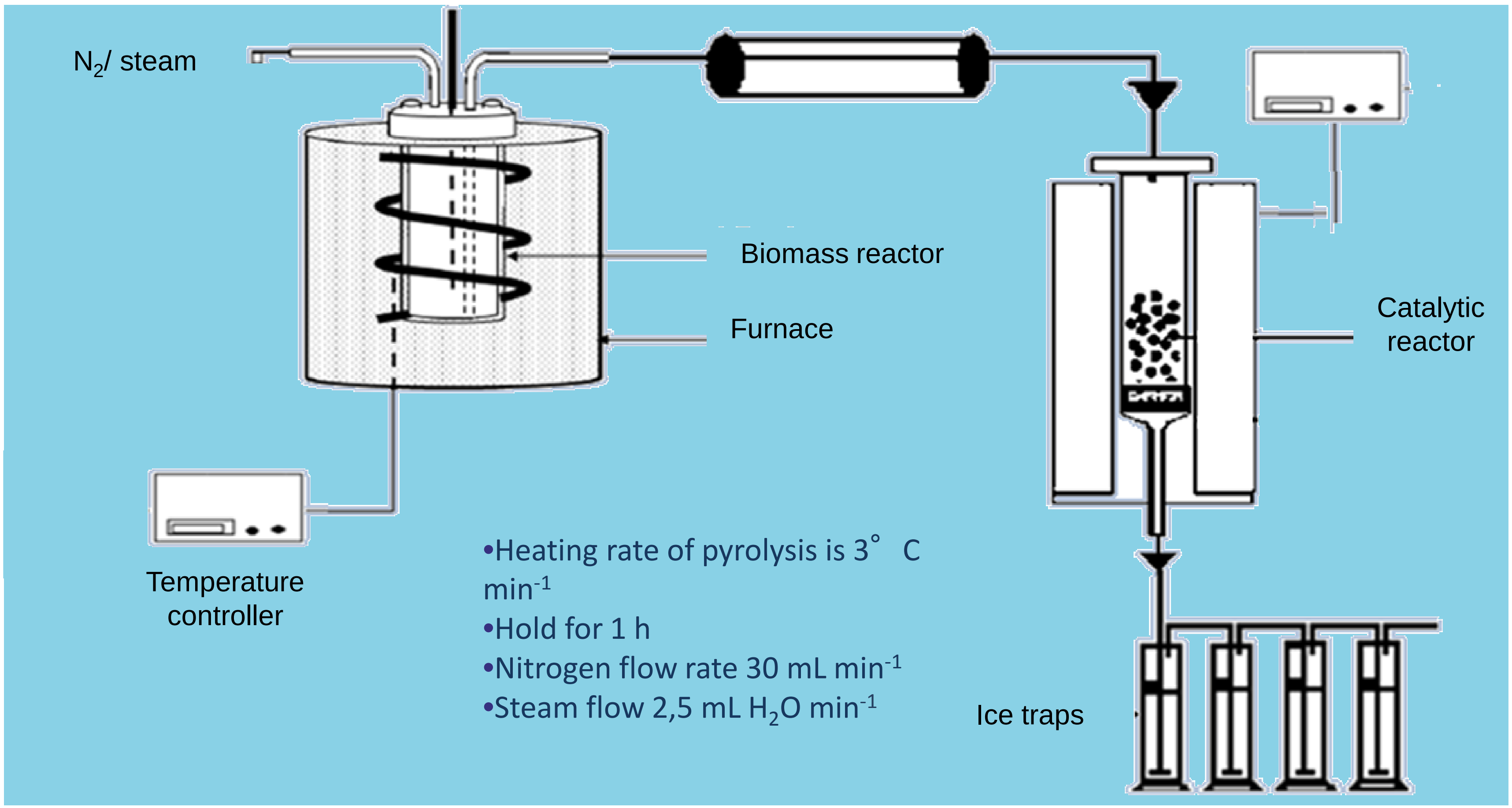
Char and char-supported nickel catalysts for secondary syngas cleanup and conditioning

Duo Wang[a,b], Wenqiao Yuan[a,*], Wei Ji[b]

STEAM REFORMING OF BIO-OIL

Experiment



- Heating rate of pyrolysis is 3° C min^{-1}
- Hold for 1 h
- Nitrogen flow rate 30 mL min^{-1}
- Steam flow 2,5 mL H_2O min^{-1}

STEAM REFORMING OF BIO-OIL

Results

BET surface areas of fresh and spent catalyst

	Fresh		Spent		
	BET surface area, m²/g	Micropore area, m²/g	BET surface area, m²/g	Micropore area, m²/g	Weight loss, % wt.
OP Char	2.7	0	420.6	303.0	28.5
Washed OP Char	27.7	4.9	381.4	301.6	14.5
10 %Ni/90 %Char	170.8	99.3	345.5	257.3	37.8
Coal Char	152.3	34.8	238.8	150.6	8.5
Washed Coal Char	48.2	27.7	212.1	138.1	7.5
10 %Ni/90 %Char	180.2	138.1	182.4	130.4	7.3

✓OP: Olive Pomace

✓Chars were obtained at 800 º C

✓Metal binding: impregnation method-700 ºC calcination under N_2 atmosphere

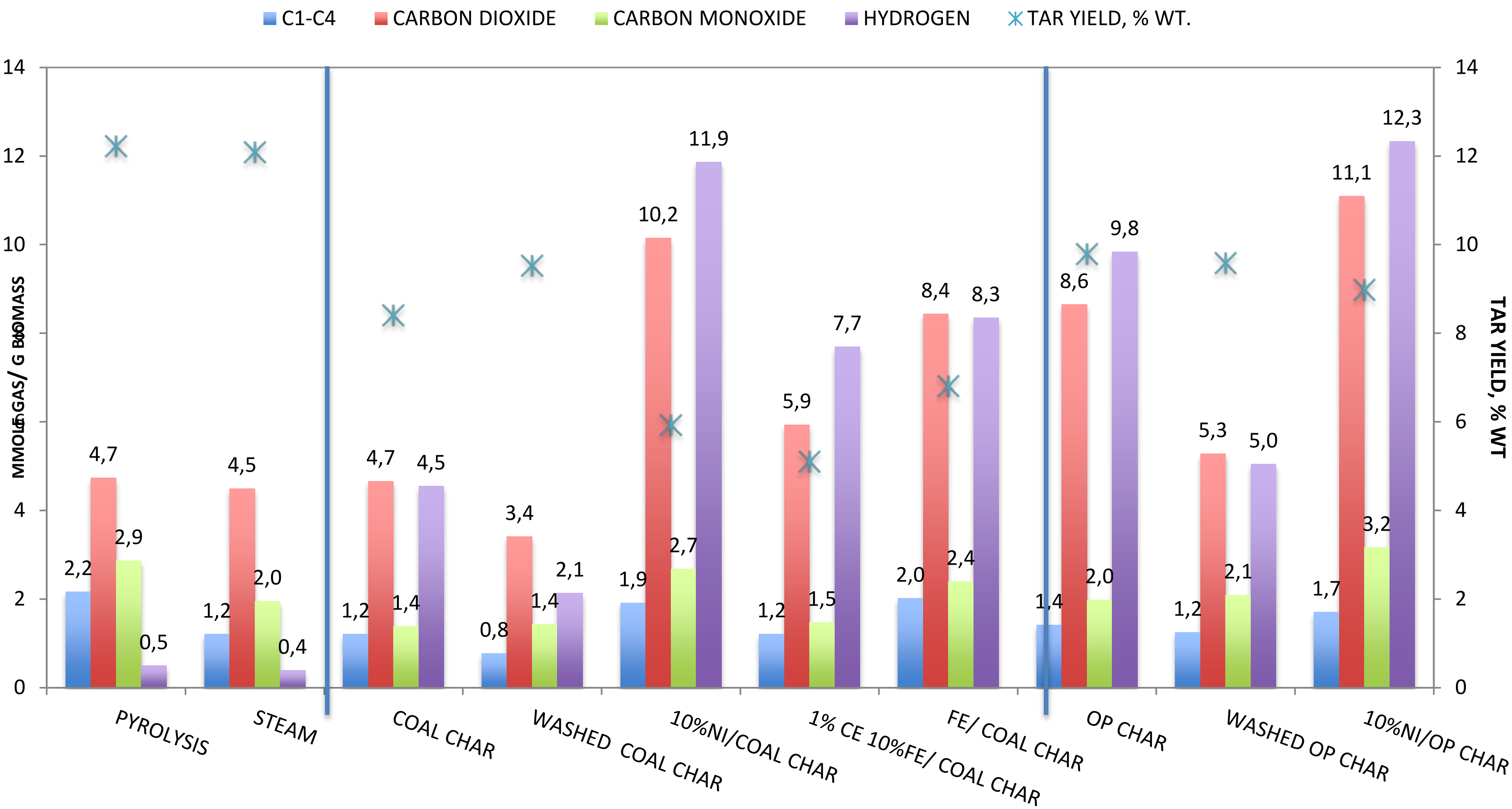
✓Ni amount as metal form

STEAM REFORMING OF BIO-OIL

Pyrolysis Temp: 500 °C

Biomass:Olive pomace

Catalytic temp: 700 °C



H_2/CO: 0.17 0.20 3.21 1.50 4.41 5.13 3.46 4.90 2.38 3.32

STEAM REFORMING OF BIO-OIL

- Steam seems unlikely to assist bio-oil decomposition without catalyst.
- Ni and Fe based chars seem to increase on both total gas yield and hydrogen amount.
- Bio-oil decomposition and water gas shift reaction took place over Ni and Fe based coal char.
- Catalysts did not considerably affect decomposition of hydrocarbon gases with steam reforming.
- Chars, especially OP char decomposed into gas products during steam reforming of bio-oil.

Thank You…

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