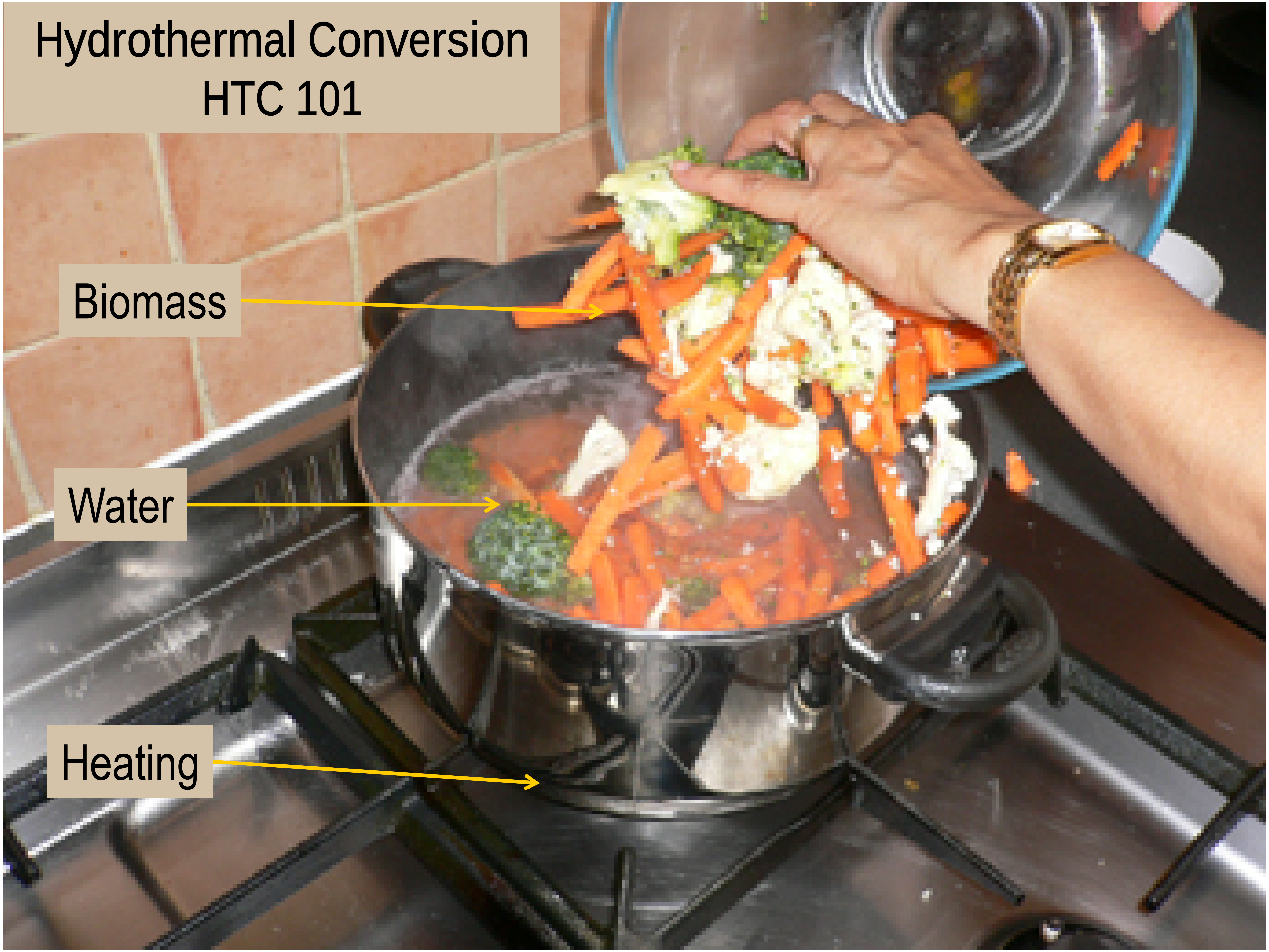
# Hydrothermal Conversion of Lignocellulosic Biomass to Biofuels and Valuable Chemicals

# Hydrothermal Conversion
# HTC 101

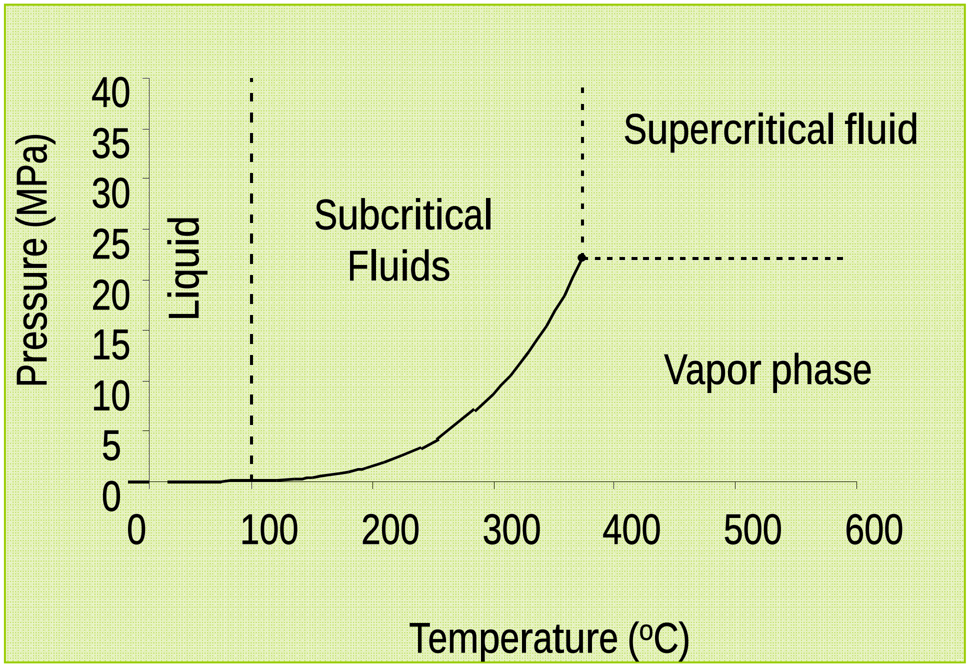


Biomass

Water

Heating

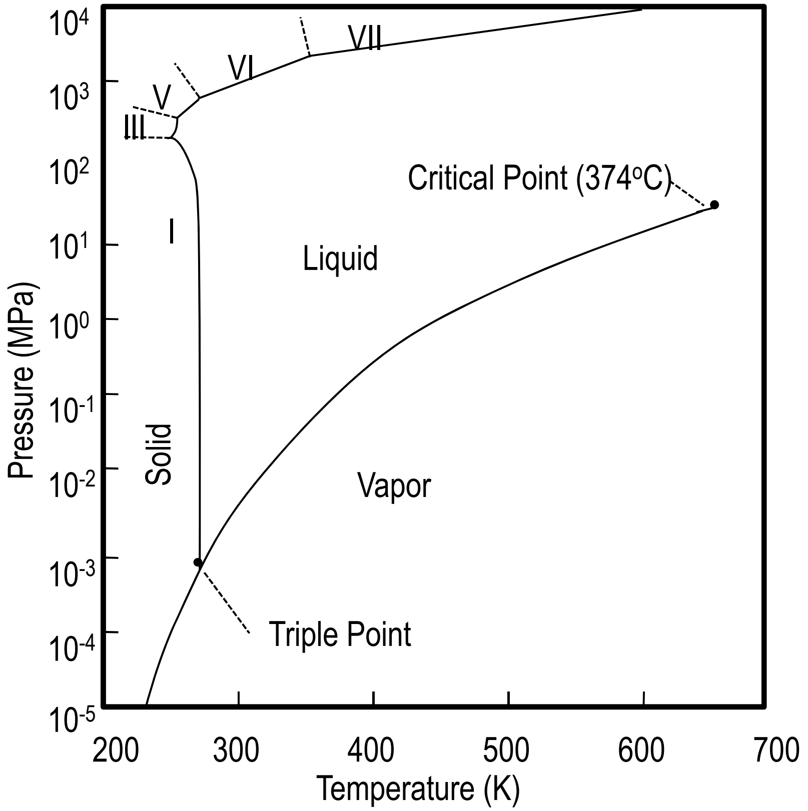
# Hydrothermal Conversion

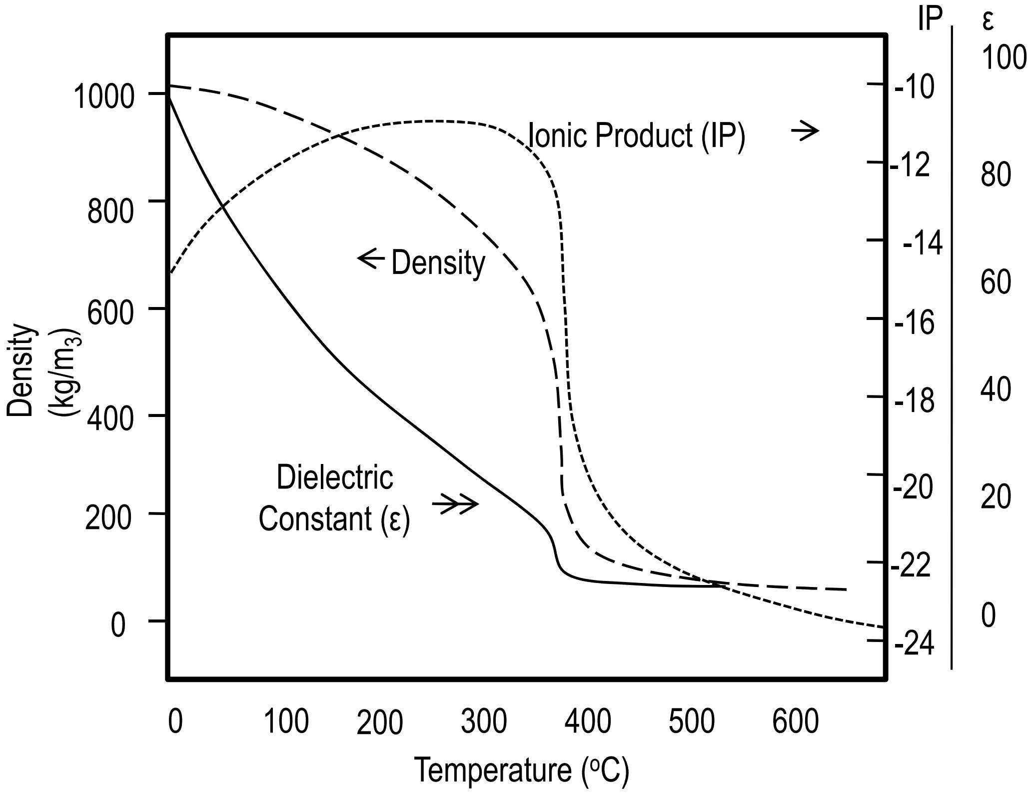


- At 200- 400 °C, 4-20MPa. water is still liquid.
- At this state, water can catalyze both acidic and basic reactions because self-dissociation of water to H+ and OH- is enhanced.

- When the temperature of water is close to supercritical point (374 °C), the phase boundary between liquid and gas disappears, and then all reactions are enhanced by the homogenous media.
- Due to these special catalytic properties of hot water, biomass HTC to bio-oil calls a great interest, but still not well studied.

# Phase Behavior of Water





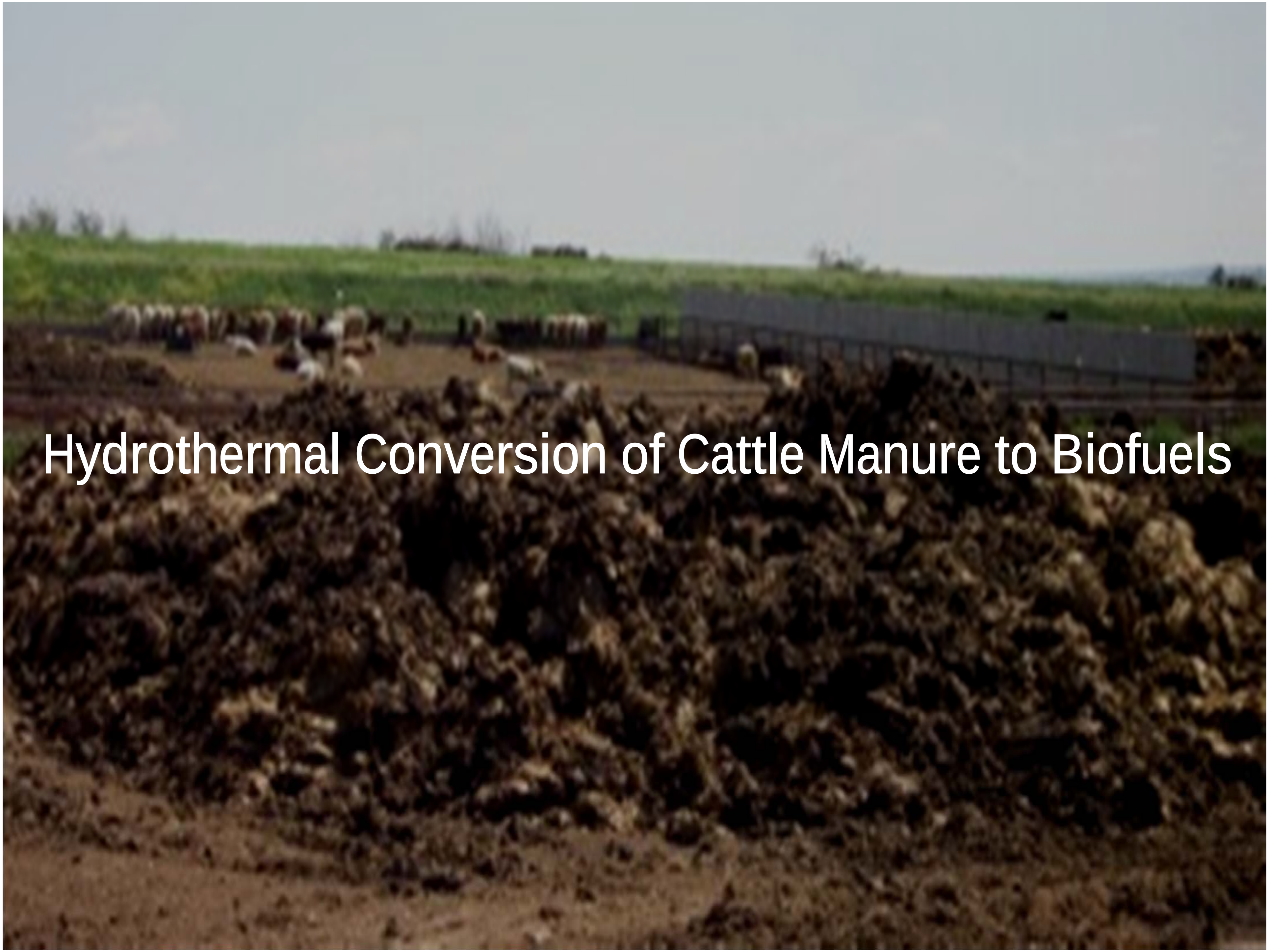
- Critical Point at 374°C
- In the subcritical region, ionic reactions are enhanced, while in the supercritical region – free radical reactions are enhanced.

# Advantages of Hydrothermal Conversion of Lignocellulosic Biomass to biofuel

- ☐ Lignocellulosic biomass
  - Most abundant feedstock
  - Low cost feedstock compared, can be zero for waste biomass like wood residue, manure, etc.
  - High yield crops (e.g. energy crops) identified
- ☐ Wet feedstock without predrying
- ☐ A thermochemical process that does not need to separate cellulose from lignin
- ☐ Can produces biogas and biooil depending on conditions

# Comparison of HTC with other technologies

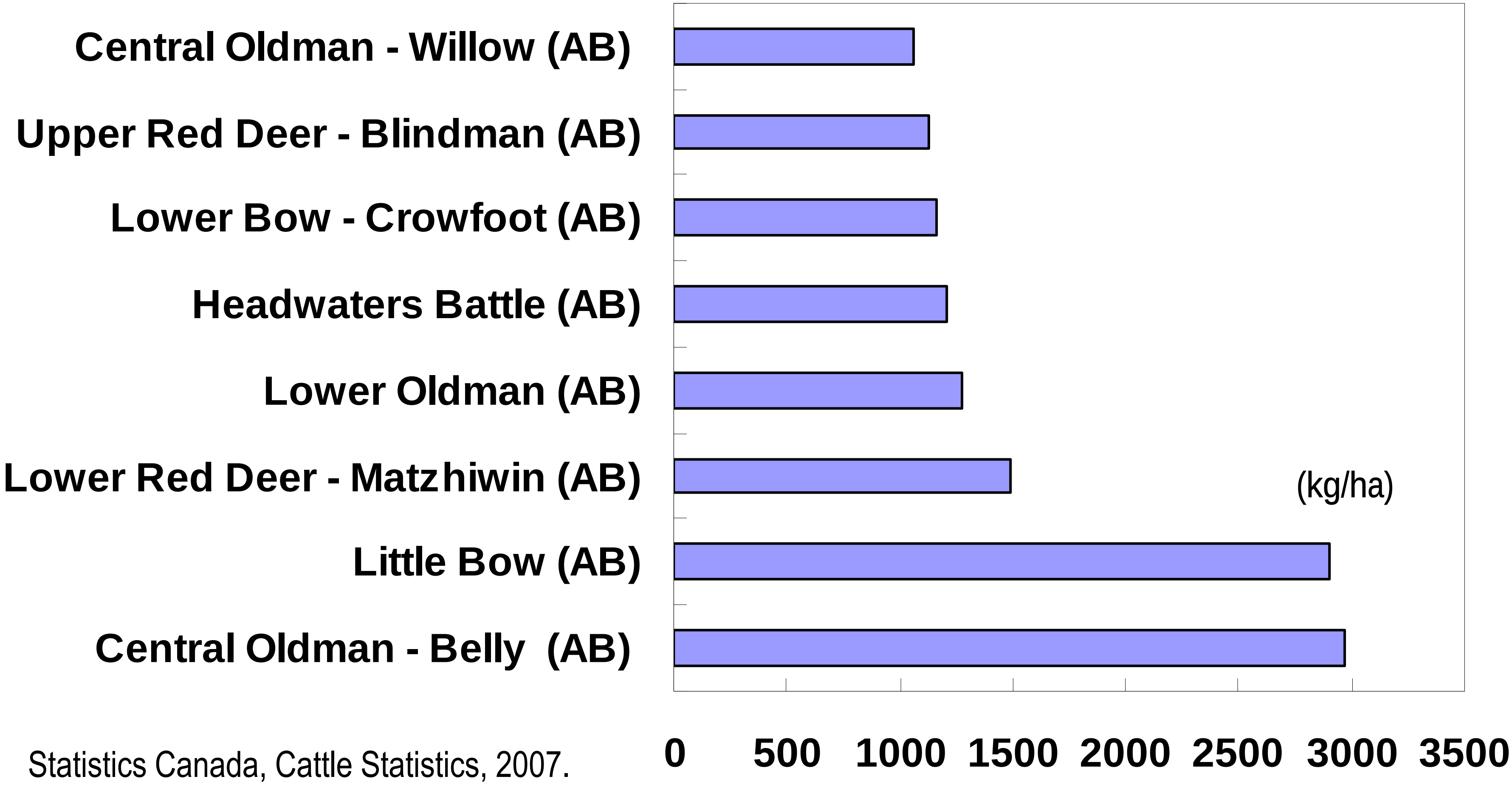
| Technologies | Conditions | Time | Main Products | Notes |
|---|---|---|---|---|
| Aerobic treatment | Ambient T and P | > 20 days | $CO_2$, Nitrate, $N_2O$ | No bioenergy |
| Anaerobic treatment | Ambient T and P | ~15 days | $CH_4$, $CO_2$ | Slowly |
| Gasification/pyrolyis | 400~600 °C | Several minutes | CH4, $H_2$, CO, $CO_2$ | Predrying required |
| **HTC** | 250 to 350 °C | 0 to 60 min | Bio-oil and $CH_4$ & $H_2$ | Without predrying |



# Hydrothermal Conversion of Cattle Manure to Biofuels

# Much cattle manure in Canada

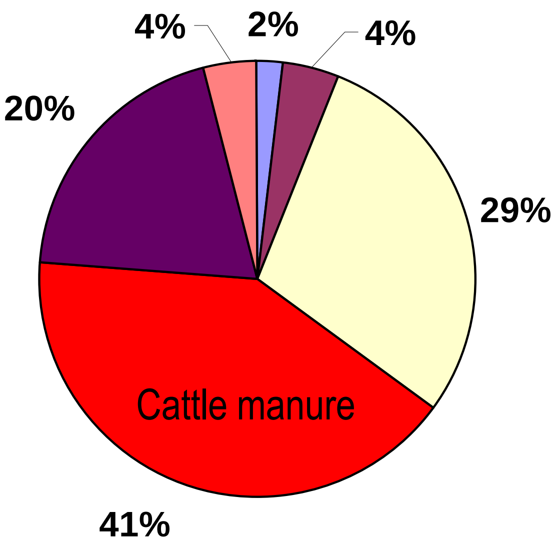
- In Canada, cattle manure production: 0.5 million tons per day [1].
- Meanwhile, more cattle manure is produced in per hectare land.



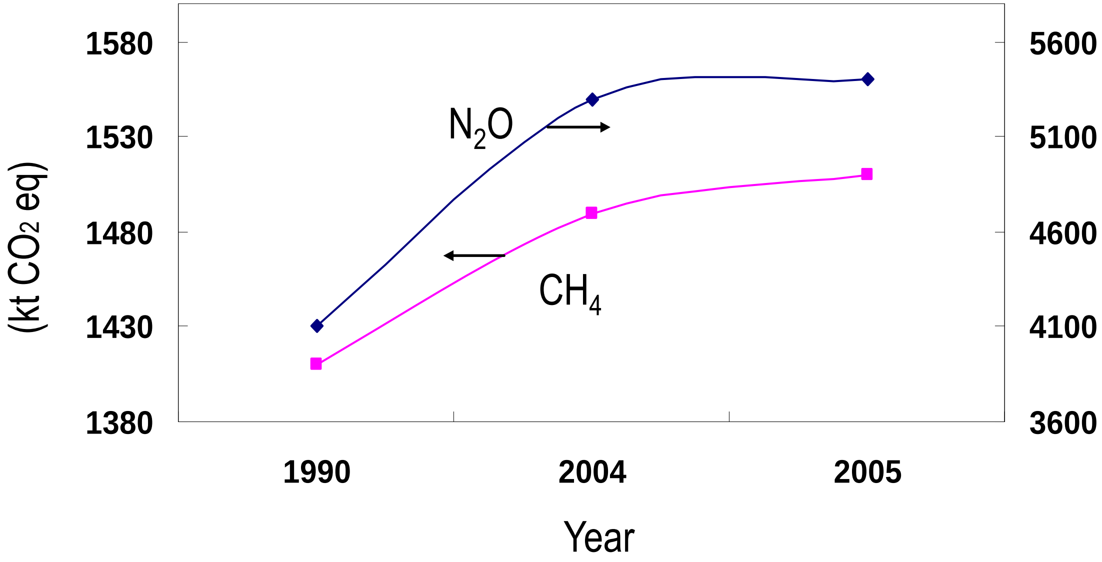
Statistics Canada, Cattle Statistics, 2007.

# Air Pollution from Cattle Manure

- Toxic gas---Ammonia
- Greenhouse gases--- $CH_4$ & $N_2O$



Ammonia emission sources
in Canada, 2005
(Environment Canada, Ammonia, 2009).



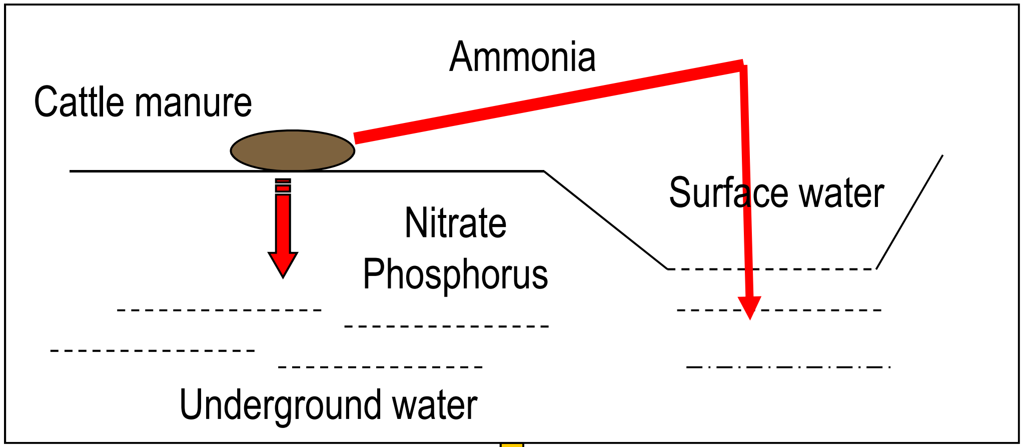
$CH_4$ and $N_2O$ emission from cattle manure in Canada .

National Inventory Report, 1990-2005: Greenhouse Gas Sources and Sinks in Canada. Environment Canada, 2007.

# Water pollution from cattle manure

- Pollutants---- Ammonia, Nitrate, and Phosphorus
- Water pollution---- Eutrophication [5]

Daniel, T. C.; Sharpley, A. N.; Lemunyon, J. L., Agriculture Phosphorus and Eutrophication: A Symposium Overview. Journal of Environmental Quality 1998, 27: 251-257



Ammonia

Cattle manure

Surface water

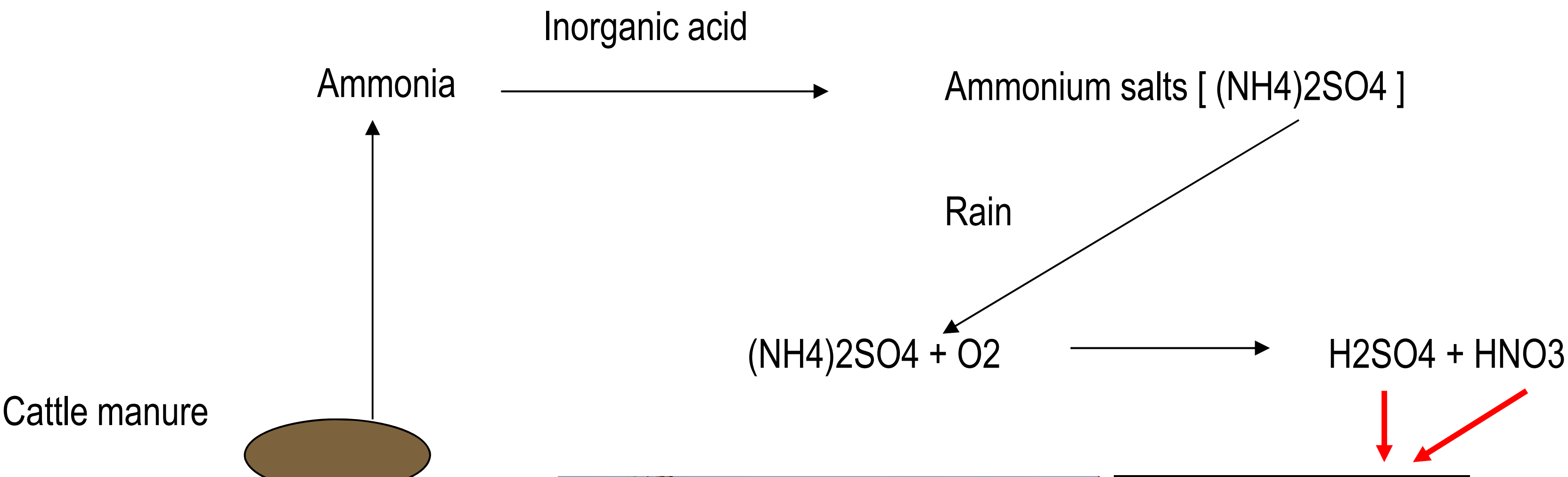
Nitrate
Phosphorus

Underground water

Eutrophication

# Soil pollution from cattle manure

- Soil pollution--- Acidification



Inorganic acid

Ammonia → Ammonium salts [ $(NH_4)_2SO_4$ ]

Rain

$(NH_4)_2SO_4 + O_2$ → $H_2SO_4 + HNO_3$

Cattle manure

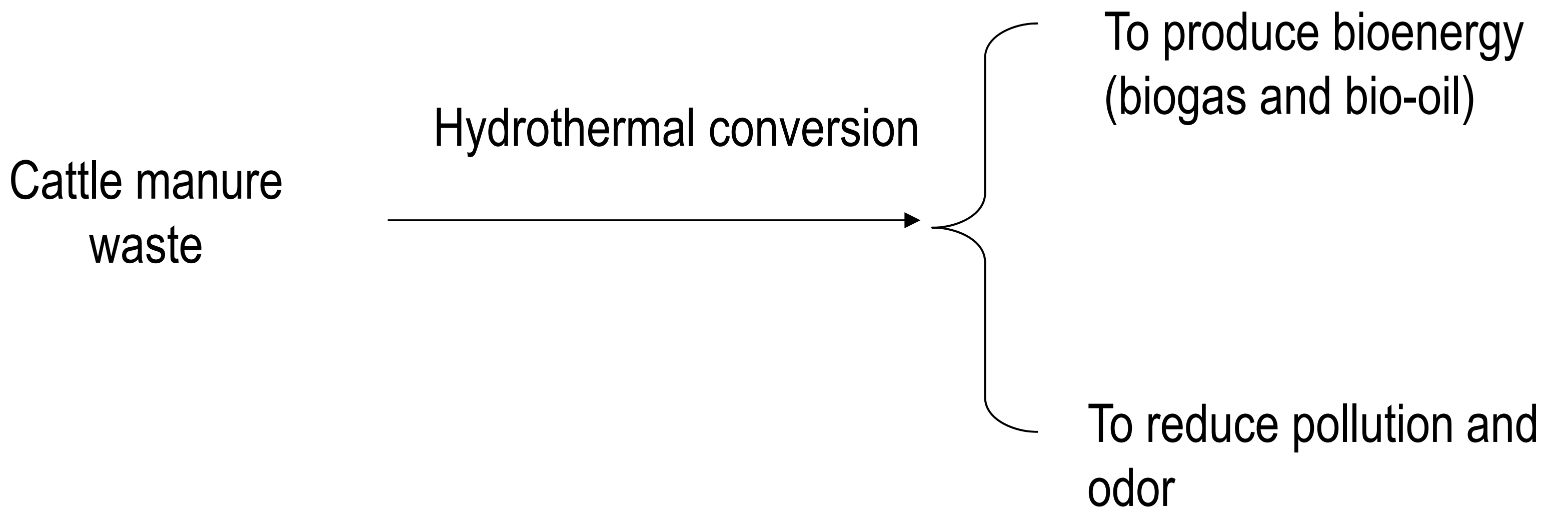
Soil

Soil

Acidified soil

Breemen, N. V.; Burrough, P. A.; Velthorst, E. J.; Van Dobben, H. F.; Wit,T. D.; Ridder, T.; Reijnders, B. H. F. R., Soil Acidification from Atmospheric Ammonium Sulphate in Forest Canopy through Fall. Nature 1982, 299:548-550.

# Overall Objectives of the Research Program



Cattle manure waste

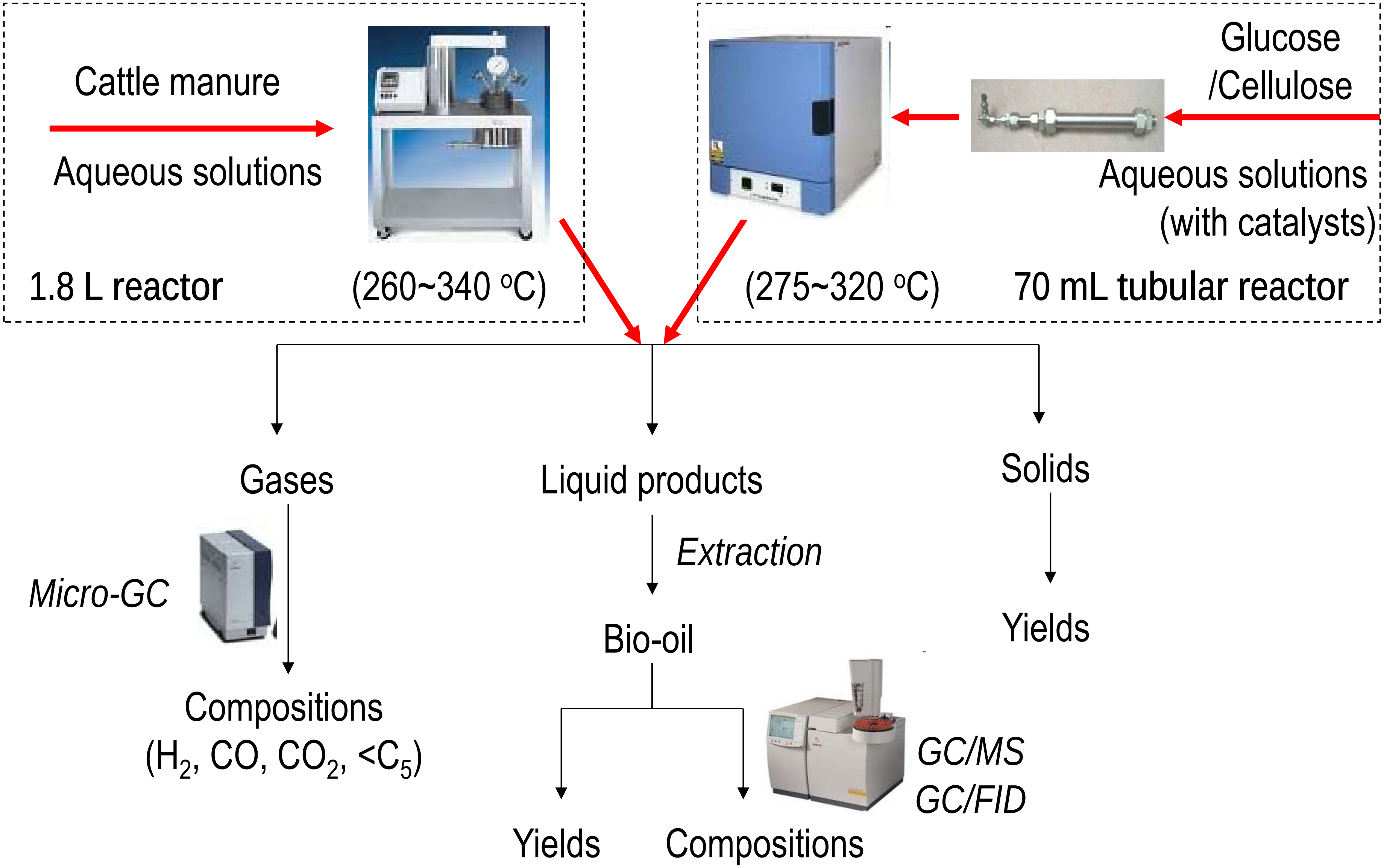
Hydrothermal conversion

To produce bioenergy (biogas and bio-oil)

To reduce pollution and odor

- Literatures have shown that swine manure, wood and grass can be converted to bio-oil by hydrothermal conversion (HTC) [7-8].
- *NO report on cattle manure in public literature*

# Overall Experimental Procedures



Cattle manure

Aqueous solutions

1.8 L reactor

(260~340 $^oC$)

Glucose
/Cellulose

Aqueous solutions
(with catalysts)

(275~320 $^oC$)

70 mL tubular reactor

Gases

*Micro-GC*

Compositions
($H_2$, CO, $CO_2$, <$C_5$)

Liquid products

*Extraction*

Bio-oil

Yields

Compositions

*GC/MS*
*GC/FID*

Solids

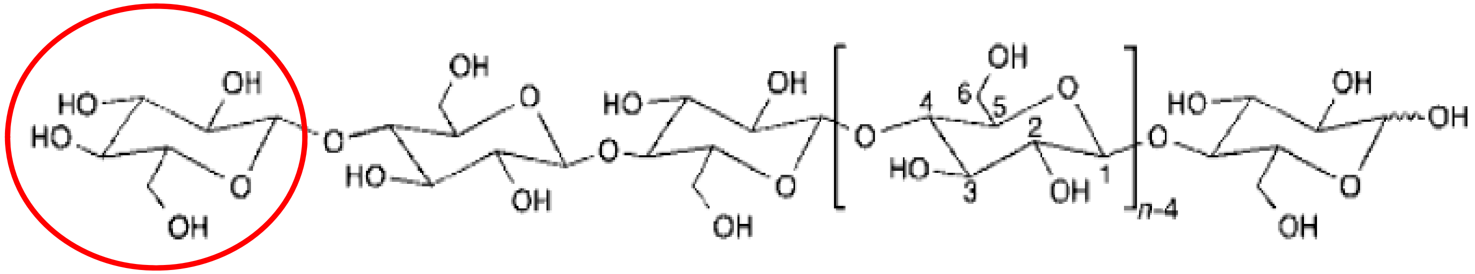
Yields

# Hydrothermal Gasification of Cellulose and Cattle Manure

## Effects of Alkalinity and Phase Behaviour

# Cellulose

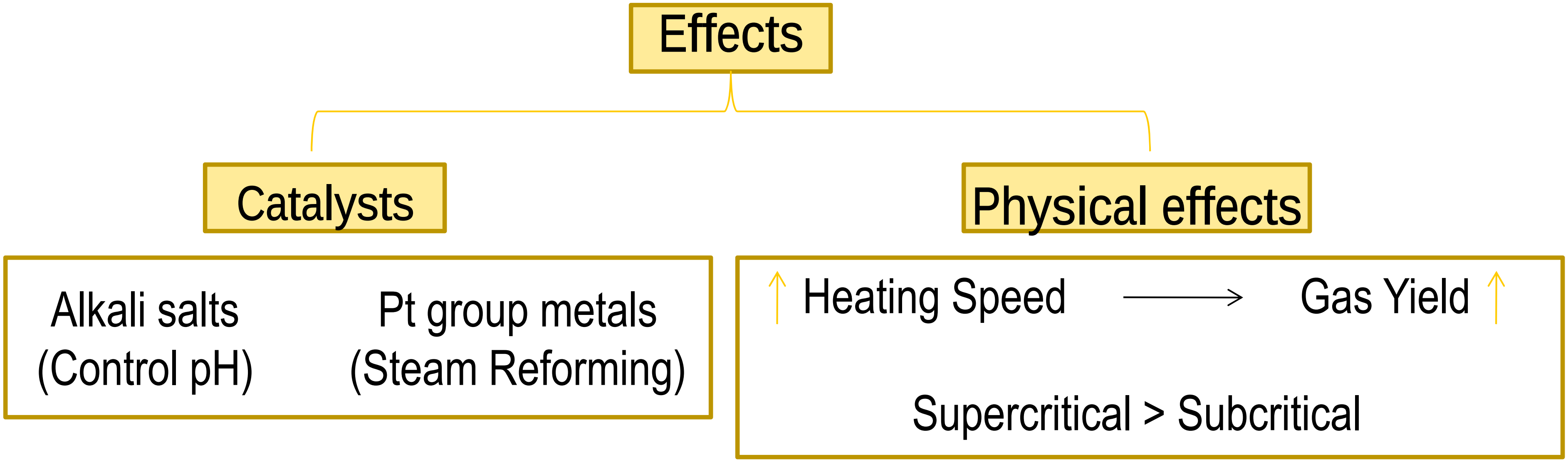
- Cellulose (a polymer of glucose) is the most abundant biopolymer globally, accounting for 1.5 x $10^{12}$ tonnes of annually available biomass. (Klemm et al, 2005)



*Glucose ($C_6H_{12}O_6$)*

$$\begin{array}{rll} & 6CO_2 + 6H_2O \rightarrow 6O_2 + C_6H_{12}O_6 & \text{Photosynthesis} \\ + & C_6H_{12}O_6 + 6H_2O \rightarrow 12H_2 + 6CO_2 & \text{Steam Reforming} \\ \hline & 12H_2O \rightarrow 12H_2 + 6O_2 & \end{array}$$

# Hydrothermal Gasification



**Effects**

**Catalysts**

Alkali salts
(Control pH)

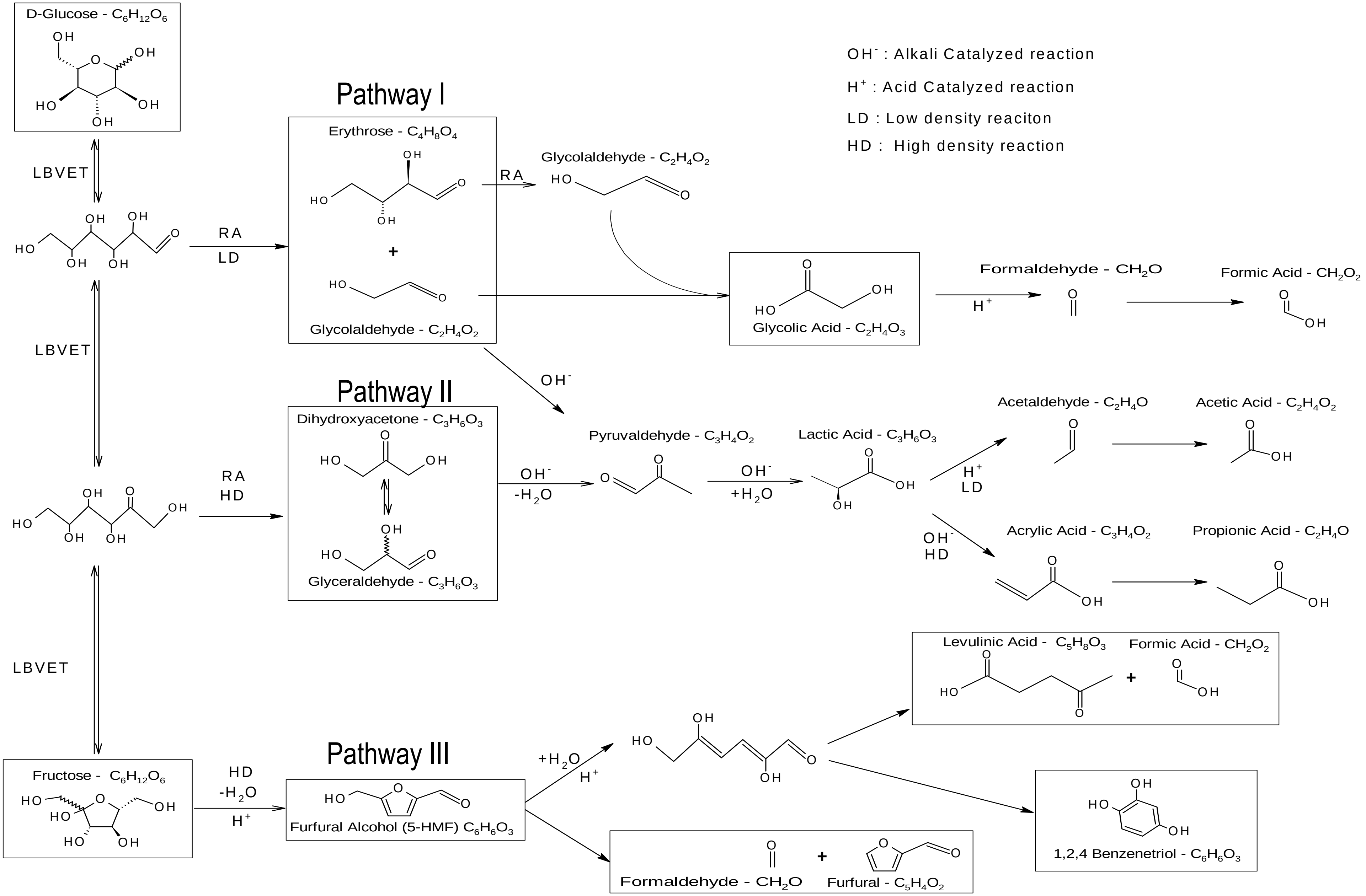
Pt group metals
(Steam Reforming)

**Physical effects**

↑ Heating Speed → Gas Yield ↑

Supercritical > Subcritical

# Cellulose Decomposition



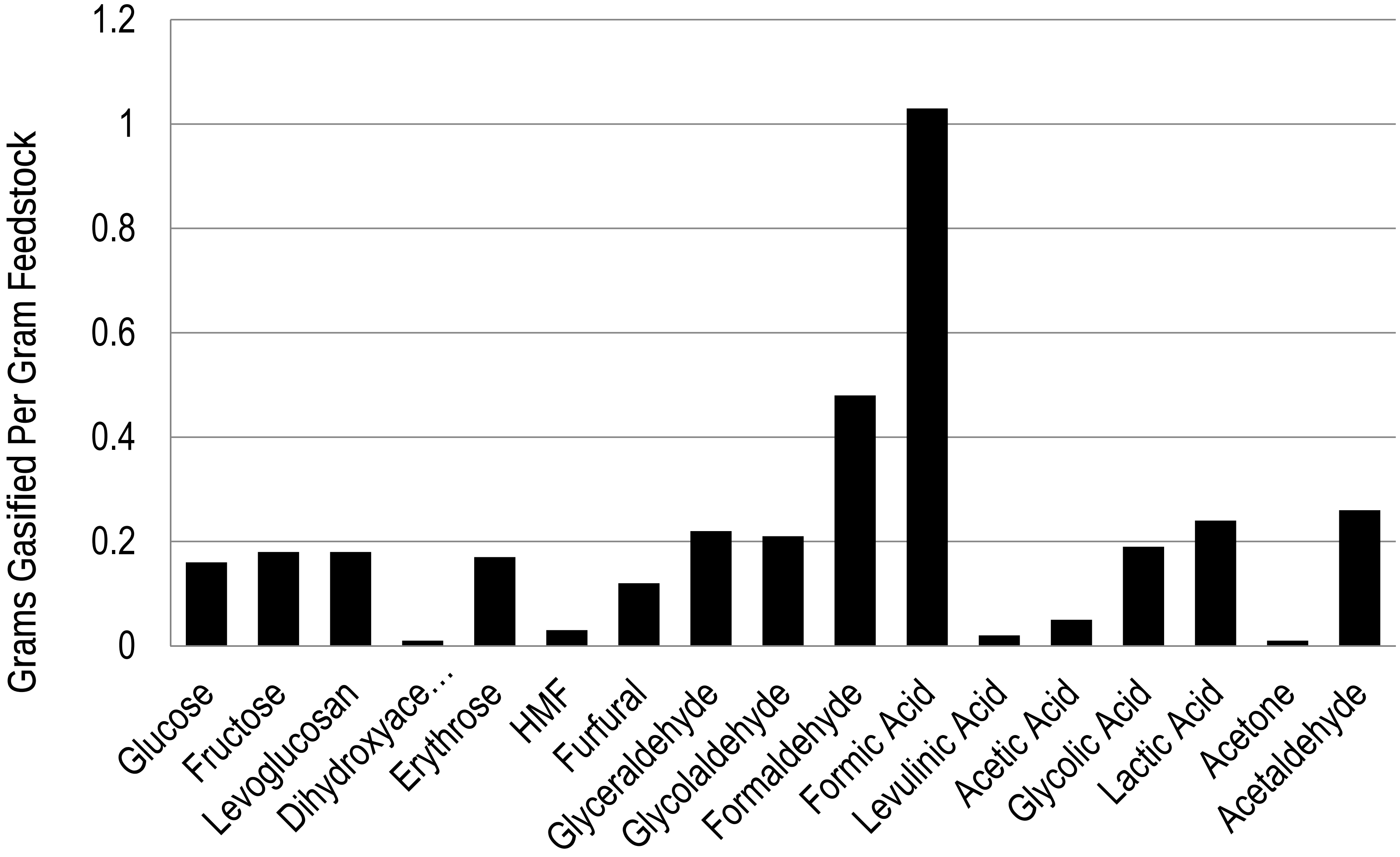
$OH^-$ : Alkali Catalyzed reaction

$H^+$ : Acid Catalyzed reaction

LD : Low density reaciton

HD : High density reaction

# All Intermediates Not Equal



Results by Knezivic et al (2009) show not all intermediates gasified as easily…

# Research Objectives and Overview

- Determine effects of alkali salt ($Na_2CO_3$) concentration on the gasification of cellulose in the presence of a Platinum group metal
- Determine effect of headspace fraction on the hydrothermal gasification of cellulose in the presence of a Platinum group metal
- Effect of alkali and a Pt group metal on the hydrothermal gasification of a mixed biomass, cattle manure.

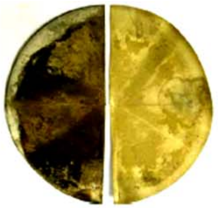
# Experimental Setup I

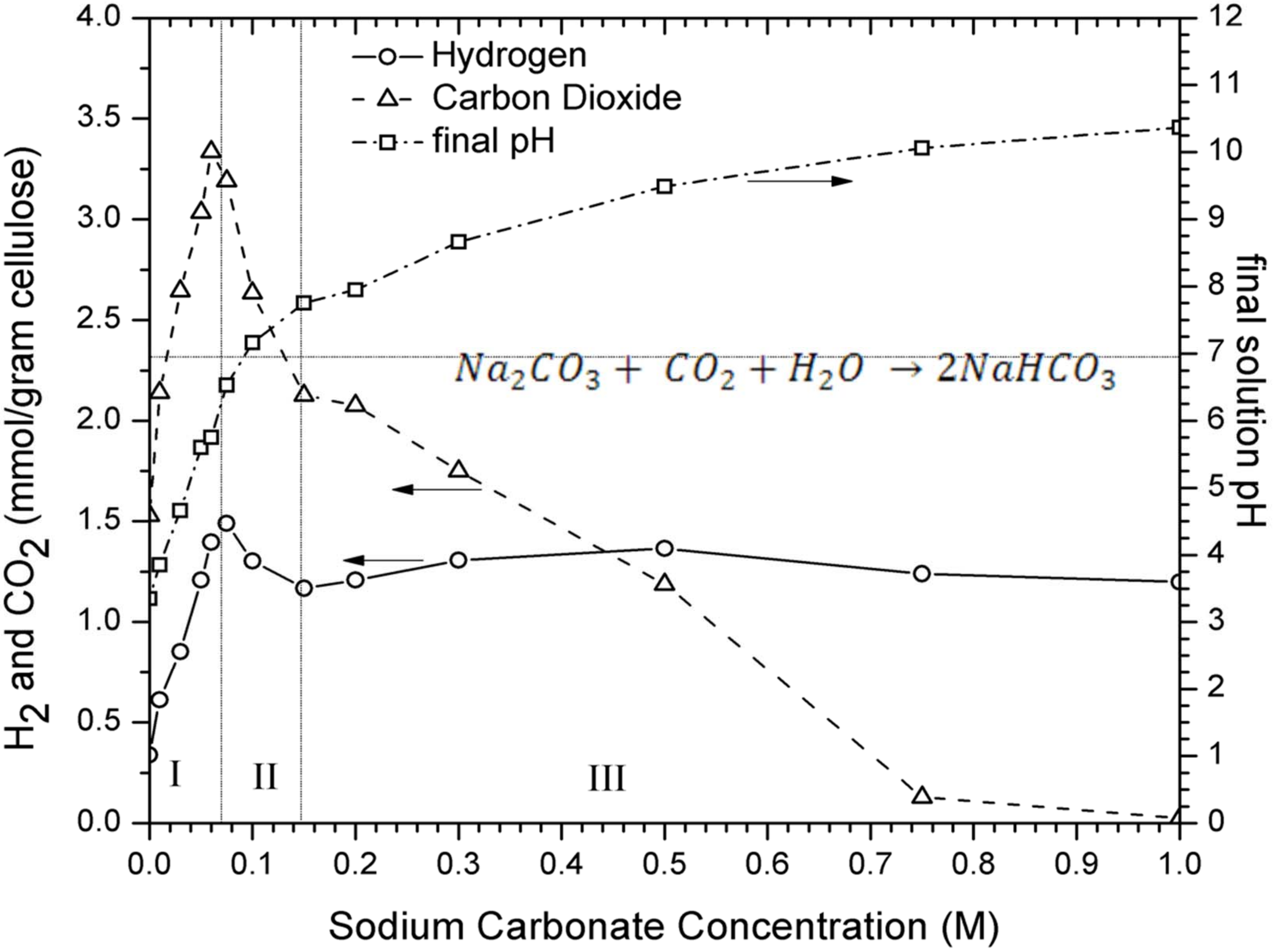
- Two batch reactors were constructed from SS 316 tubing. The reactor volume was 69mL.
- Reactors heated by Muffle Furnace

- Gas composition determined by micro gas chromatography (micro-GC)

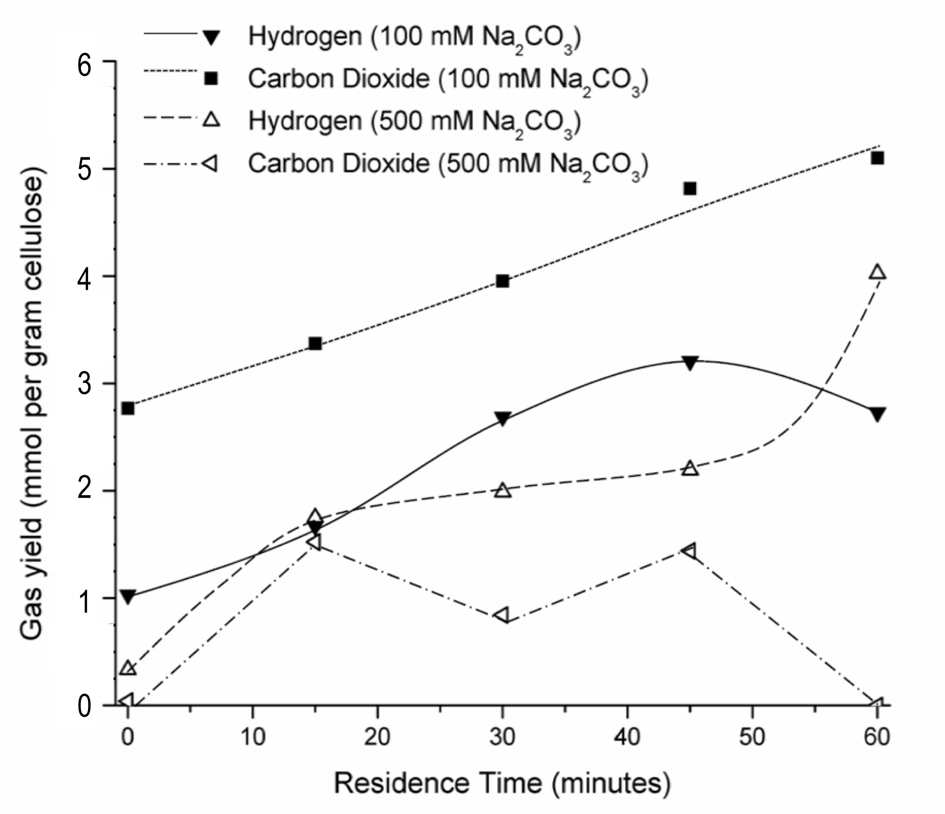
- Liquid phase composition determined by gas chromatography with a flame ionization detector (GC-FID)

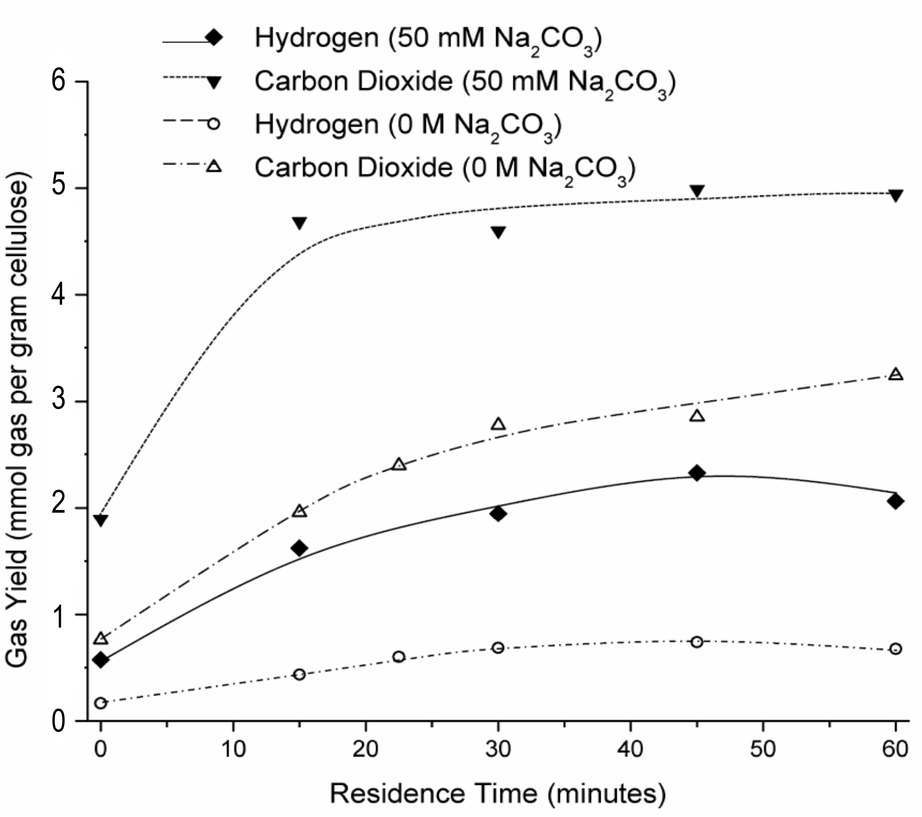
# Effects of Alkalinity with 5% Pt/$Al_2O_3$ catalyst





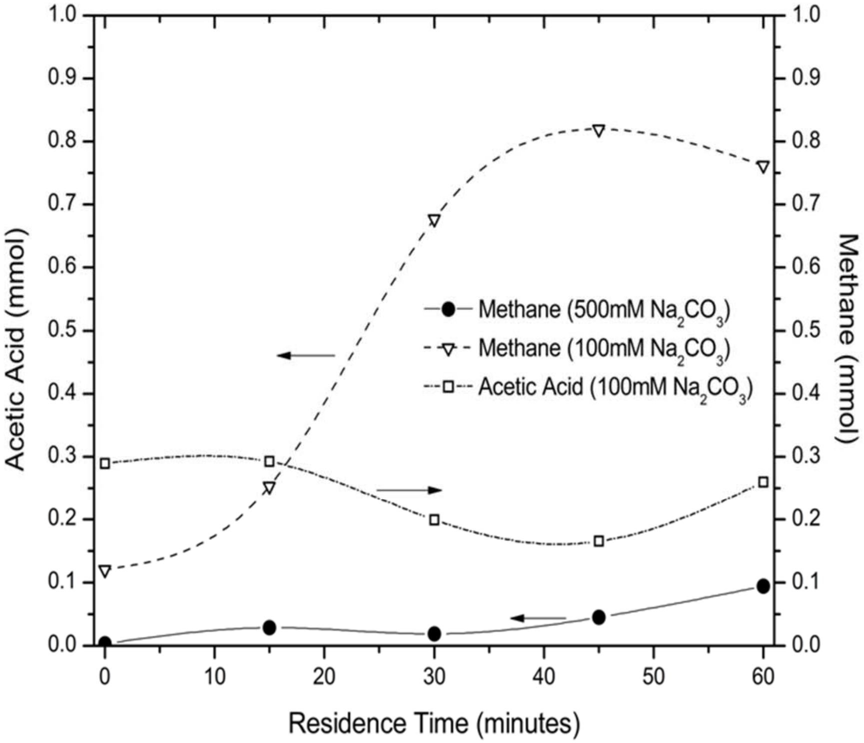
# Effects of Residence Time

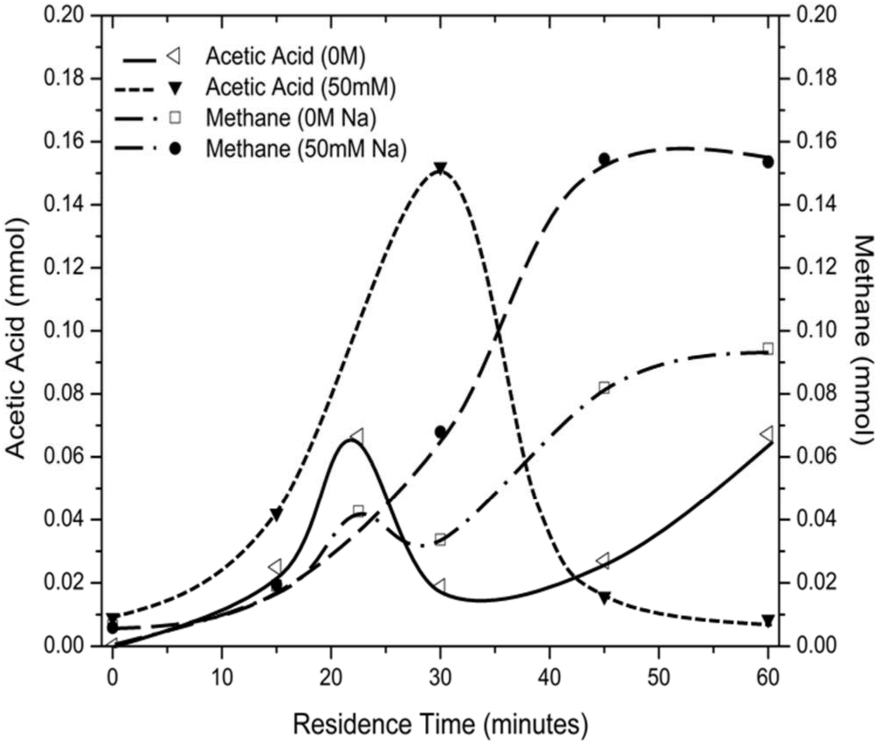




- Sodium Carbonate (alkaline pH) increase both carbon dioxide and hydrogen production

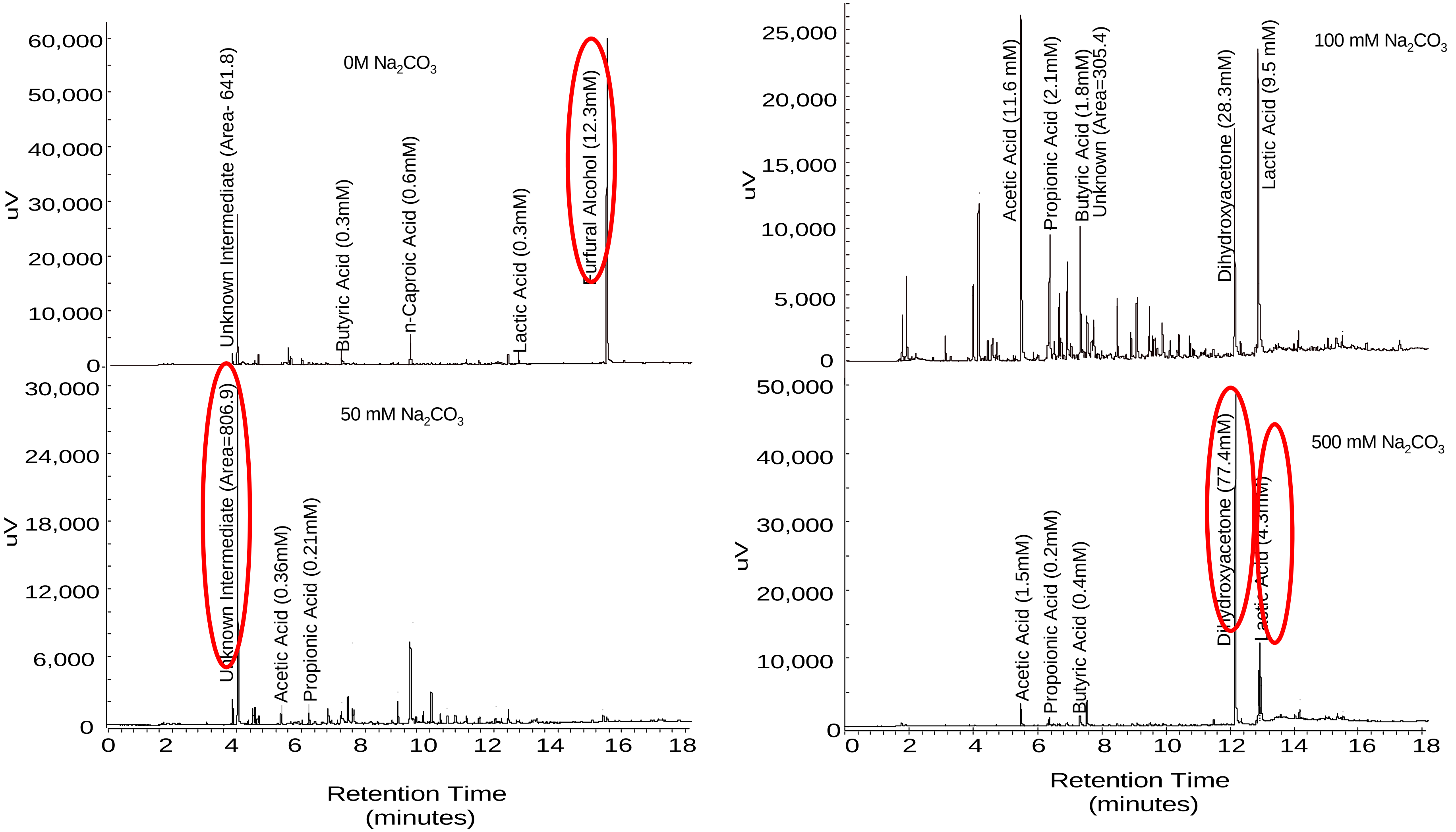
# Acetic Acid and Methane





- As more acetic acid was produced, increasing amounts of methane were found in the solution.
- Highest yields of acetic acid (and methane) were found in 0.1M sodium carbonate solution.

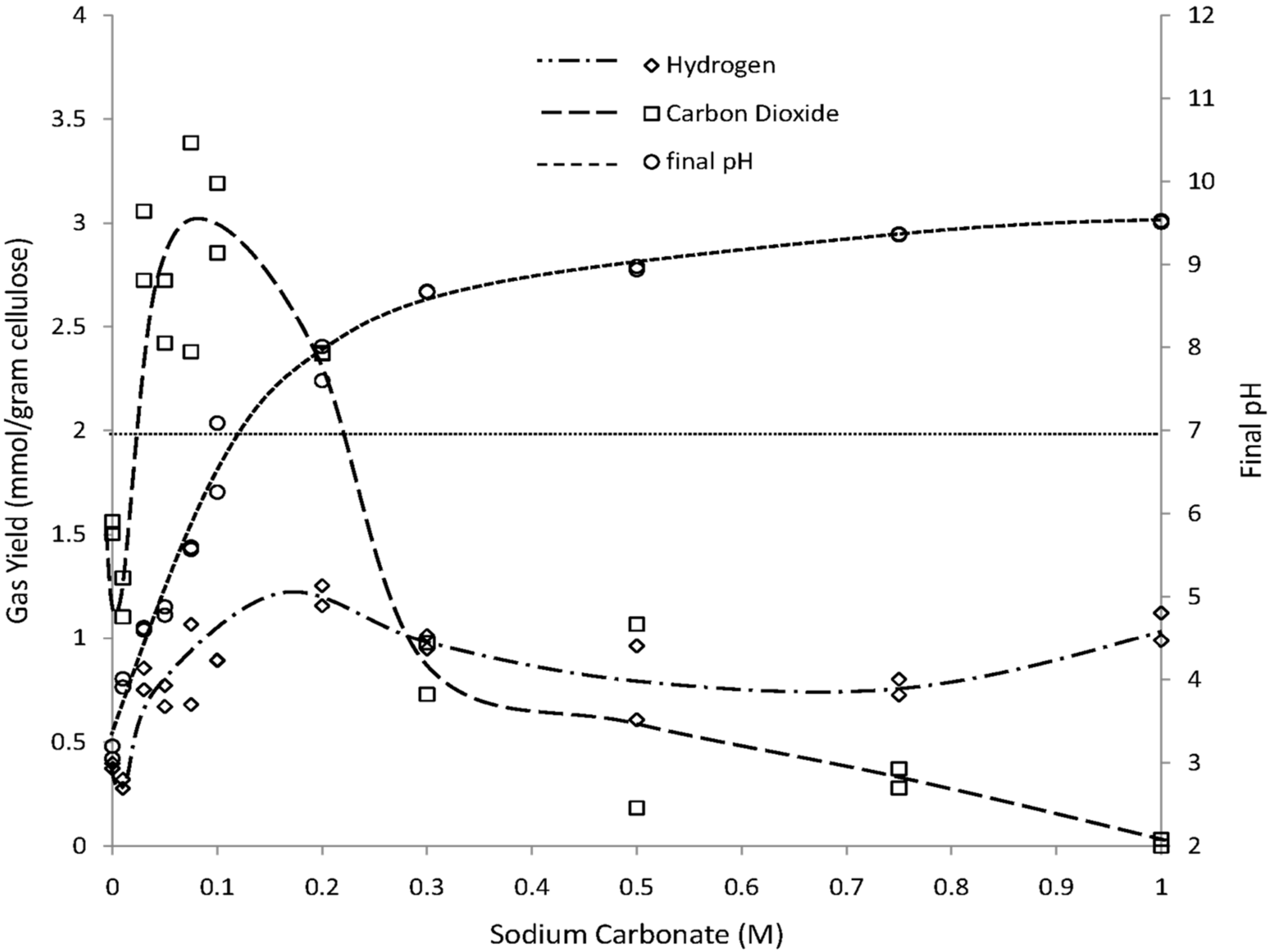
# Liquid Phase Analysis



0M $Na_2CO_3$ – More Furfural Alcohol (HMF)

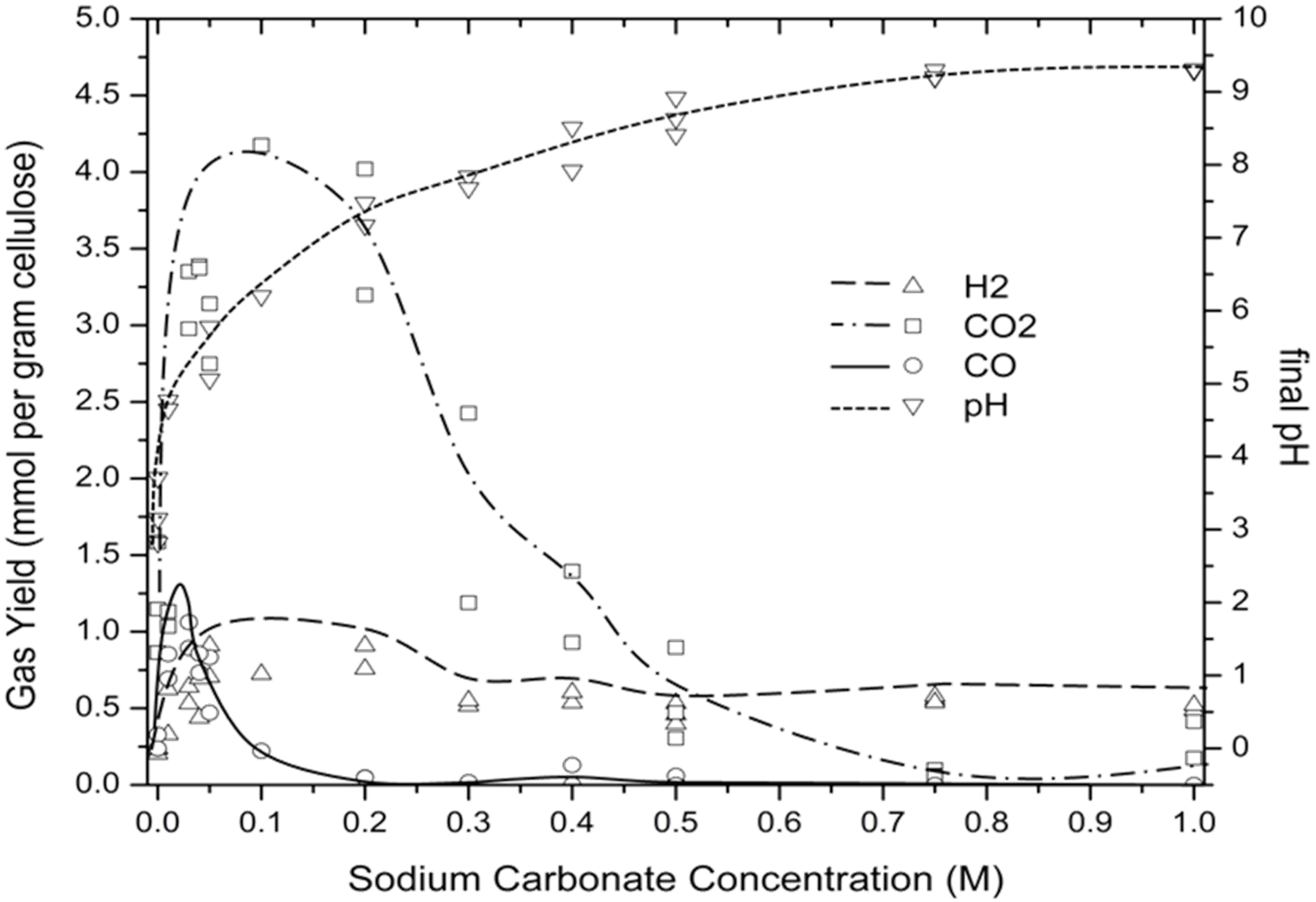
500 mM $Na_2CO_3$ – More Dihydroxyacetone and Lactic Acid

# Alkalinity Effects with 5% Pt/$SiO_2$



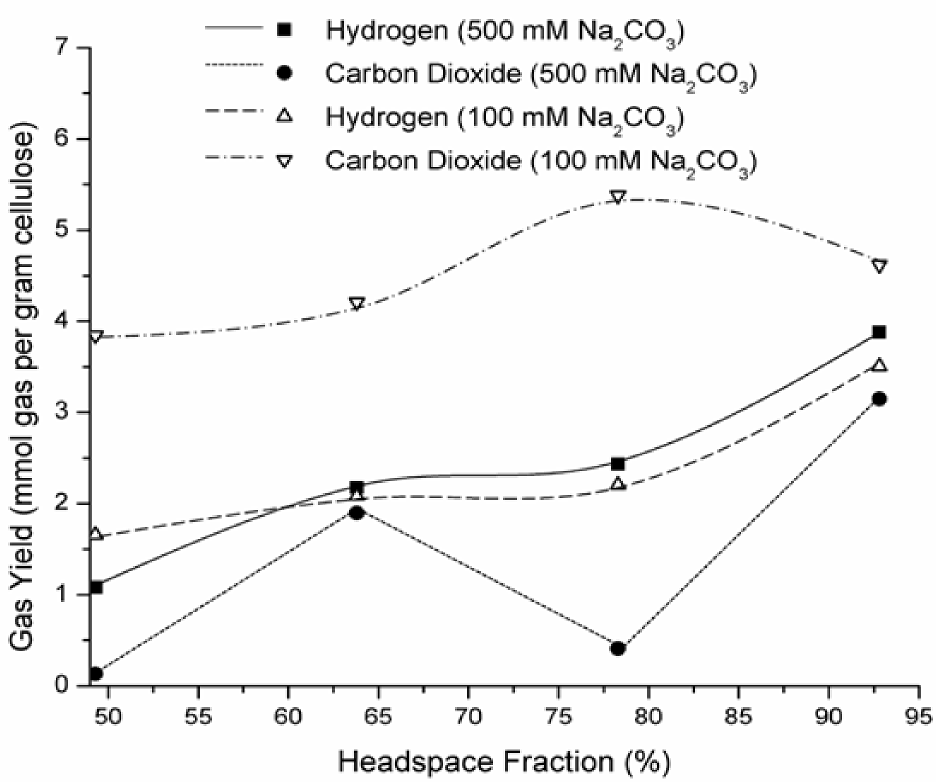
Similar but more variable results were obtained using a  5% Pt/SiO2 catalyst.

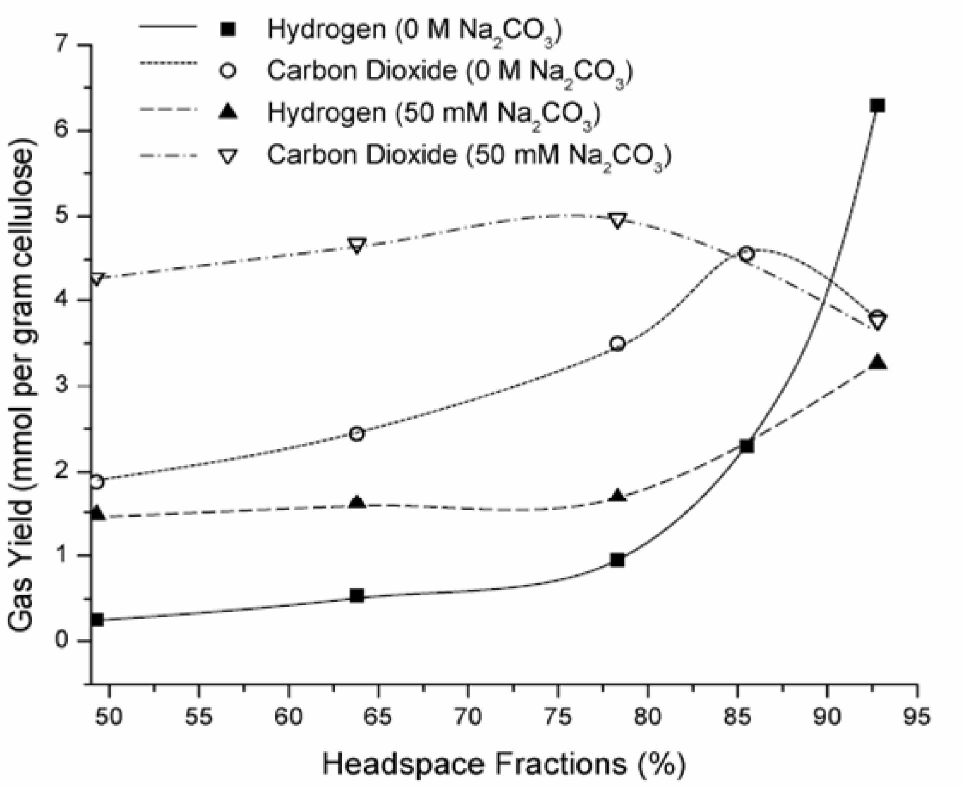
# Alkalinity Effects with 1% Pt/$Al_2O_3$



With a higher loading of 1% Pt/Al2O3, carbon monoxide became an important product under low alkalinity.

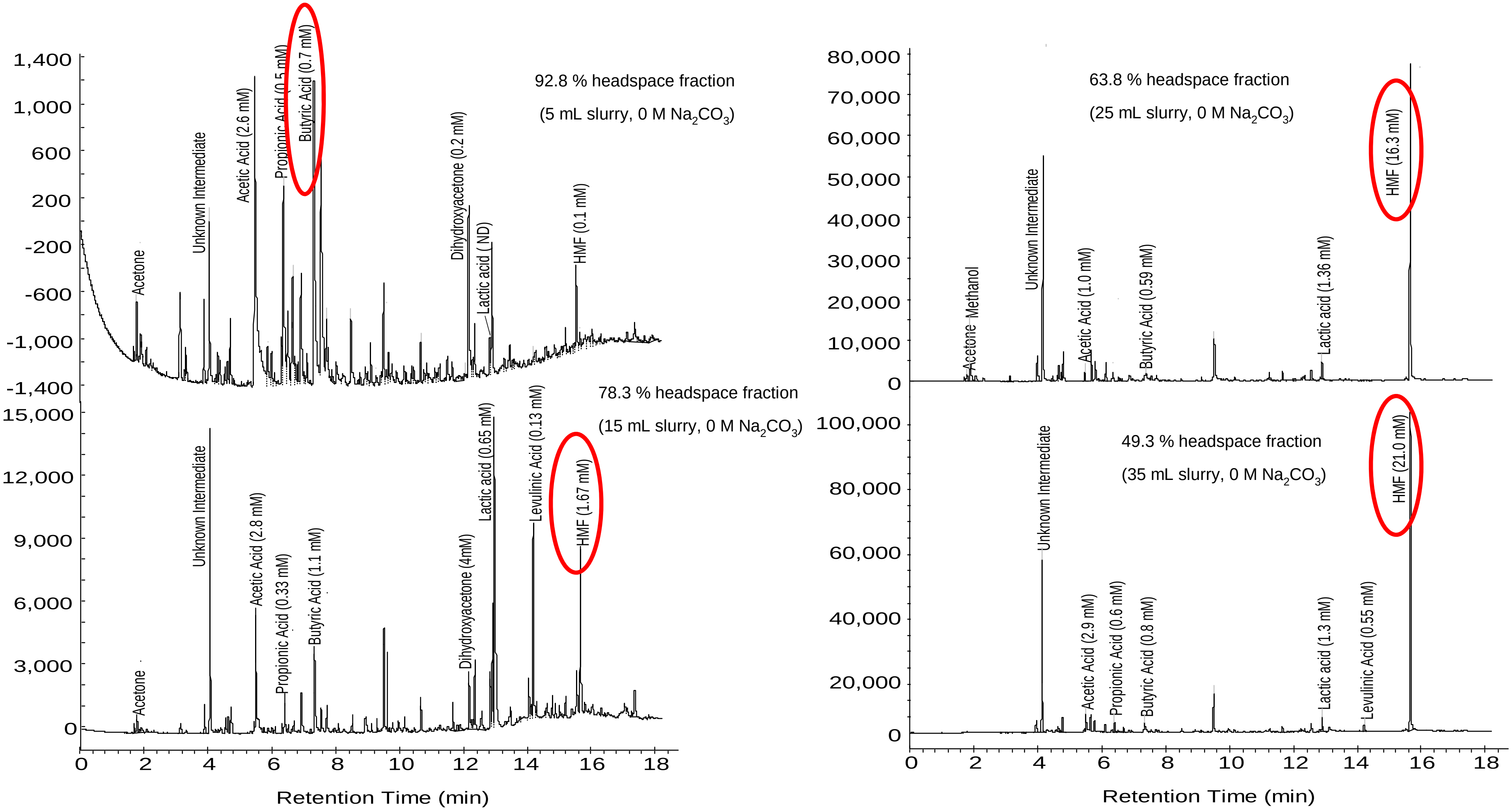
# Effect of Headspace Fraction





- As headspace fraction increased, hydrogen increased.
- Magnitude of increase was dampened when sodium carbonate was added.

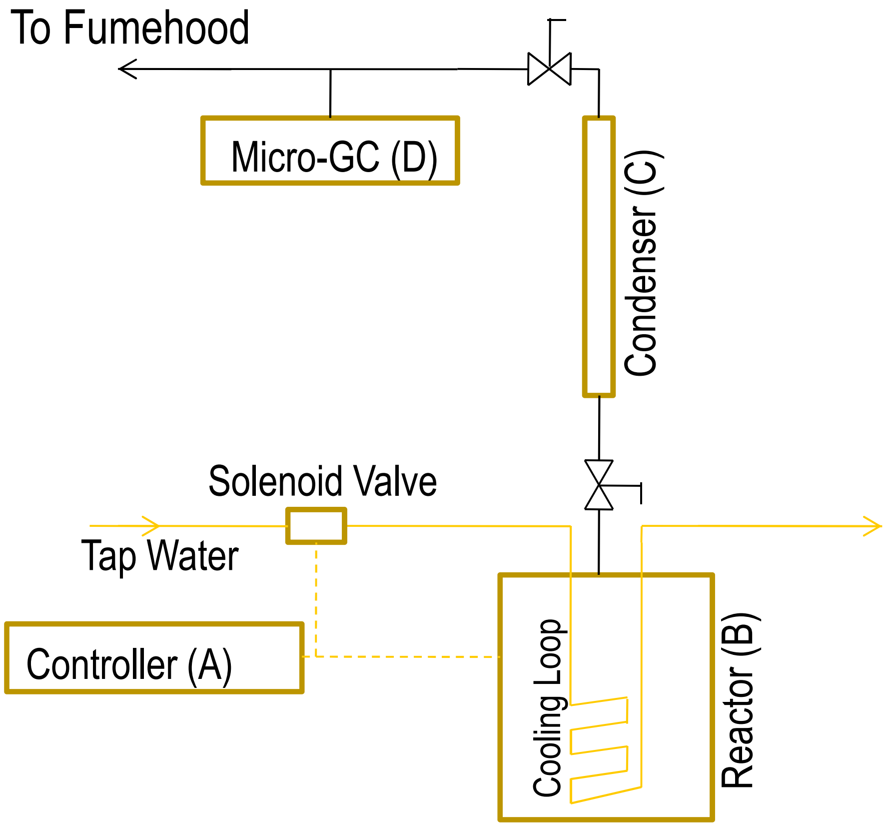
# Liquid Phase Analysis

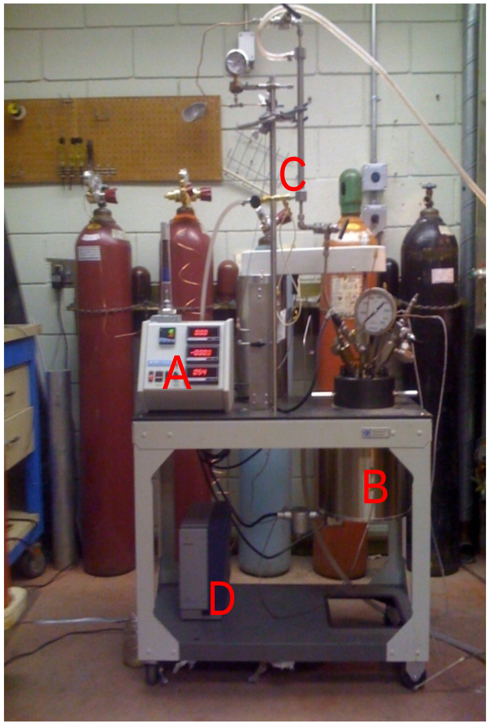


- HMF suppressed as the headspace fraction increased
- At highest headspace fraction, butyric acid most abundant

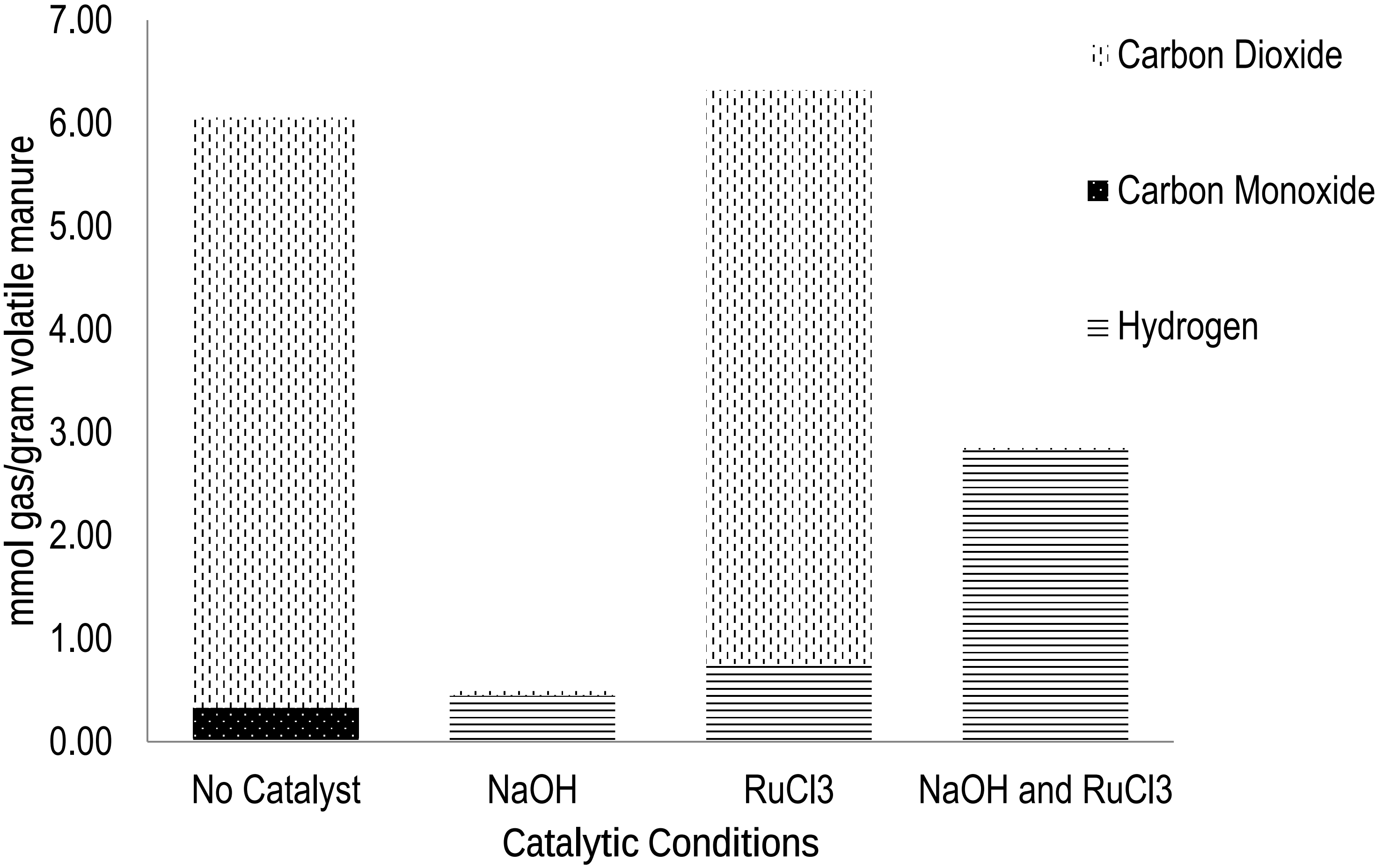
# Experimental Setup II

- 1.8 L batch reactor (SS316), Parr Instrument Company
- Gas composition was analyzed by micro-GC





# Cattle Manure Test Results



Experiments with Cattle Manure show synergy between the $RuCl_3$ and the basic NaOH catalysts

# Discussion – Effects of Alkalinity

- Three Distinct Regions of Alkalinity
  1. Region I – HMF suppression
  2. Region II – Change to Basic Solution pH
  3. Region III – Formation of Bicarbonates from Carbon Dioxide
- Peak in Hydrogen when using Pt/$SiO_2$ catalyst occurred at higher alkalinity (200 mM as opposed to 75mM)
- Liquid Phase changes from HMF (0M $Na_2CO_3$) , to lactic acid and dihydroxyacetone
- Methane likely to be related to the decarboxylation of acetic acid
- Significant interaction between $RuCl_3$ and NaOH catalysts

# Discussion – Effects of Headspace Fraction

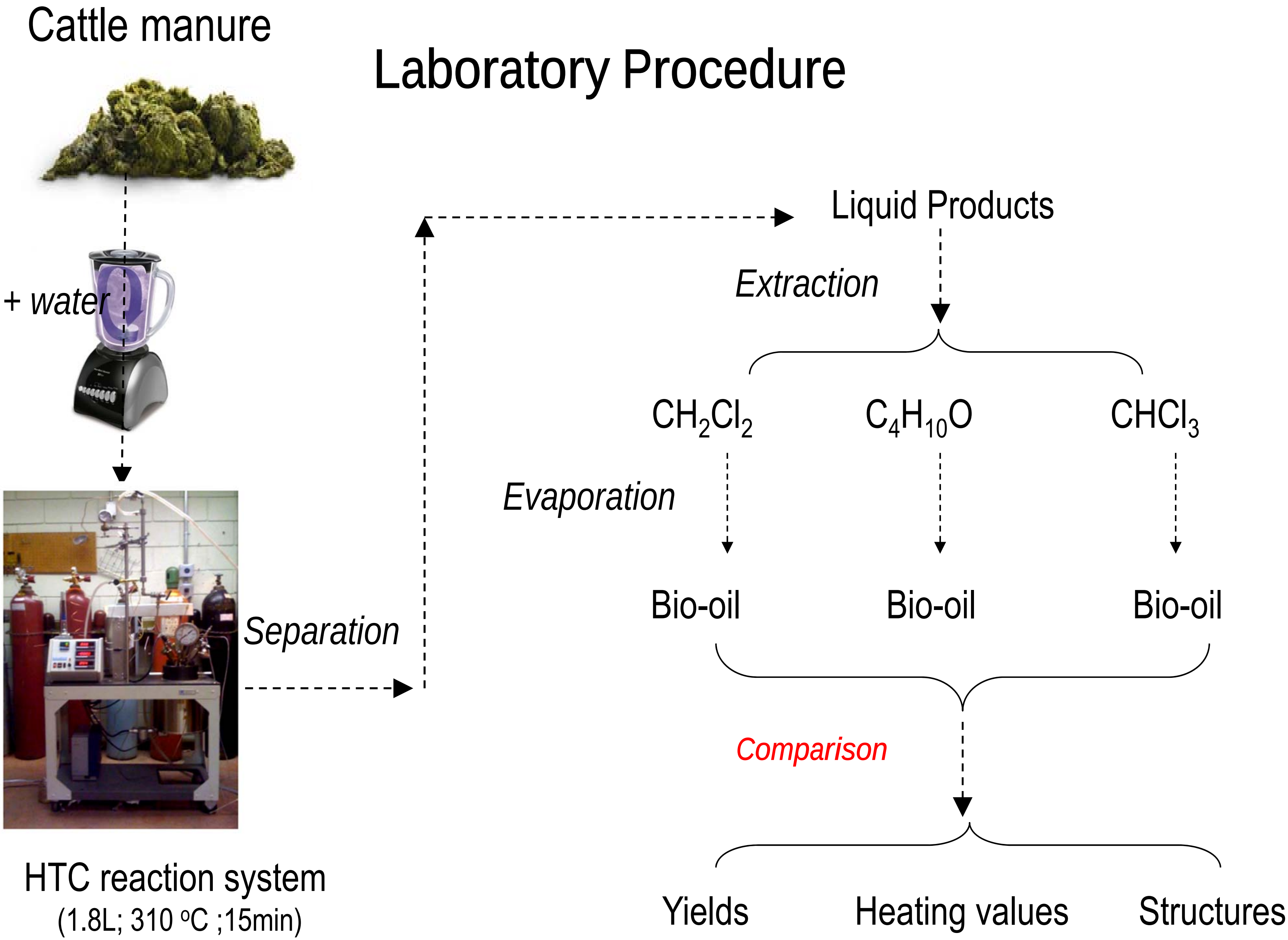
- Higher headspace fractions (vapour fractions) enhanced gas production, the effect was most significant without the addition of sodium carbonate
- In general, decreasing headspace fraction resulted in a decreased concentration of detected chemicals.
- Under the most successful conditions (92.8% headspace fraction, no $Na_2CO_3$), butyric acid relatively significant chemical in the liquid phase.

# Conclusions

- More facile pathways for gasification available under high headspace fraction, without the addition of alkali salt sodium carbonate.
- Acetic Acid appears to be a likely source for produced Methane
- Decomposition of Cellulose through HMF produces little gas
- Decomposition pathway has large impact on gasification yield and composition

# Hydrothermal Conversion of Cattle Manure to Biooil

# Laboratory Procedure



Cattle manure

+ *water*

HTC reaction system
(1.8L; 310 °C ;15min)

*Separation*

Liquid Products

*Extraction*

$CH_2Cl_2$ $C_4H_{10}O$ $CHCl_3$

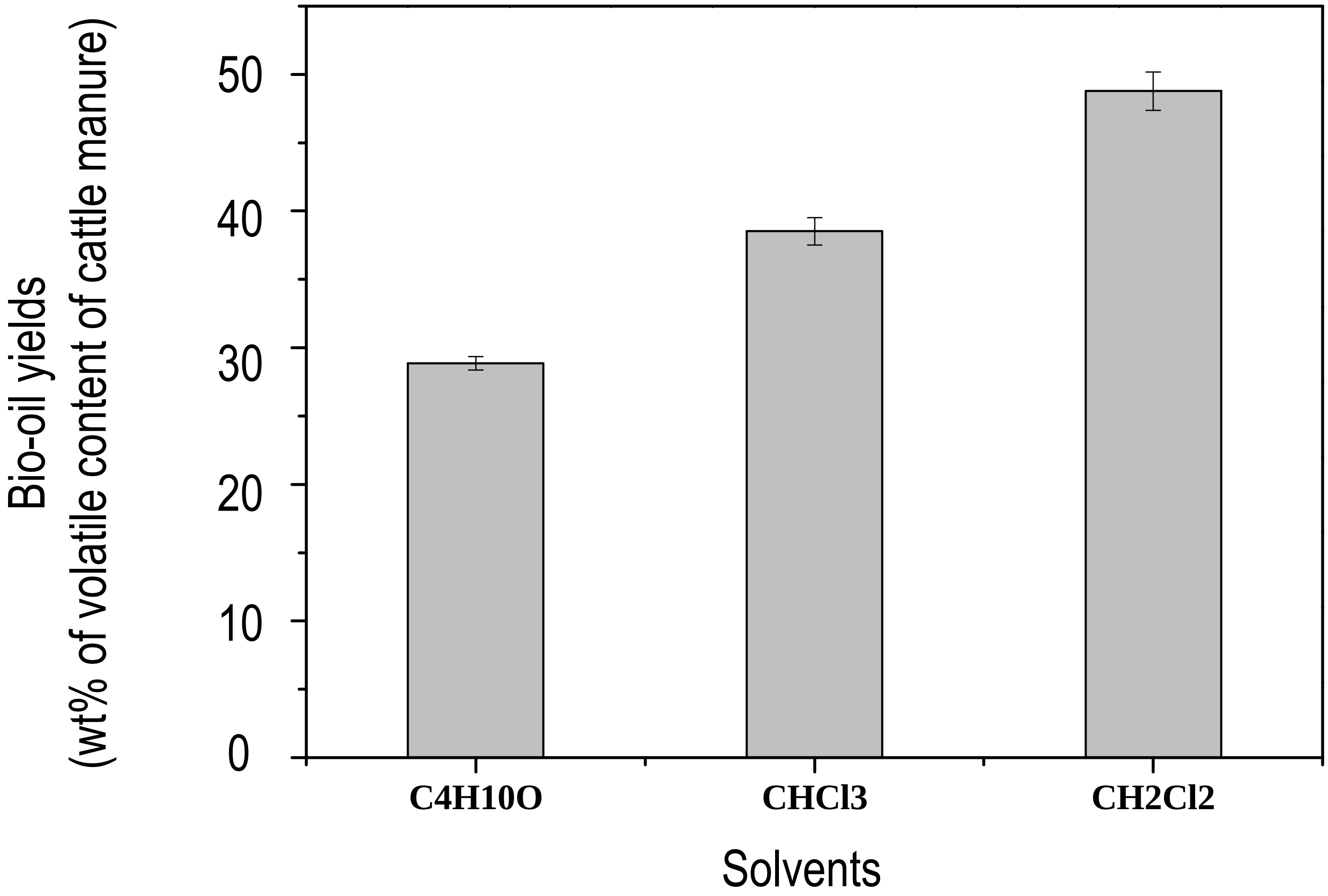
*Evaporation*

Bio-oil Bio-oil Bio-oil

*Comparison*

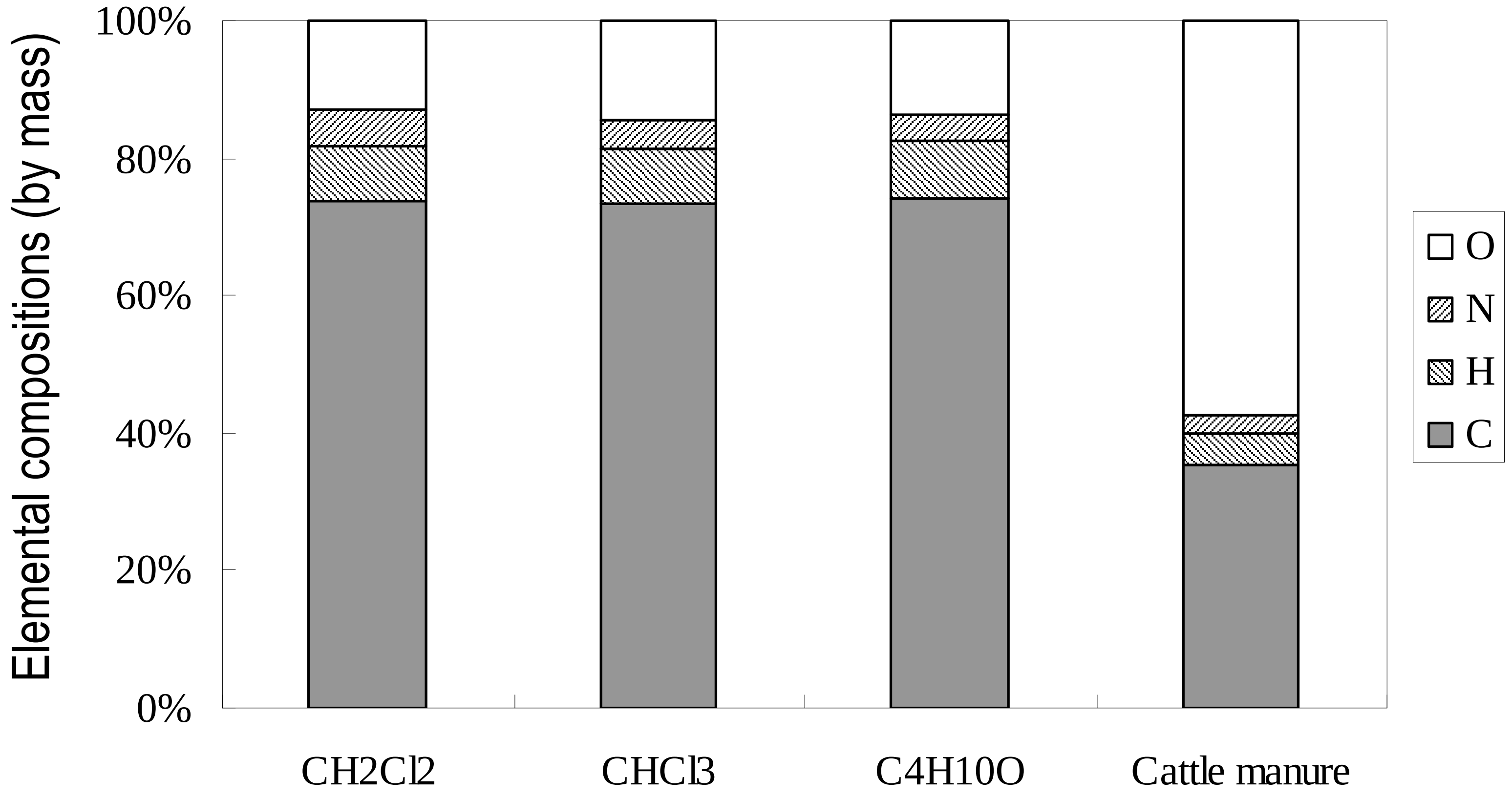
Yields Heating values Structures

# Effects of solvents on bio-oil yields



(Conditions: 125g of cattle manure, 500g of water, 0.5 mol of NaOH, residence time of 15 min, and 0 psig initial pressure of CO)

# Effects of solvents on elemental compositions of bio-oil

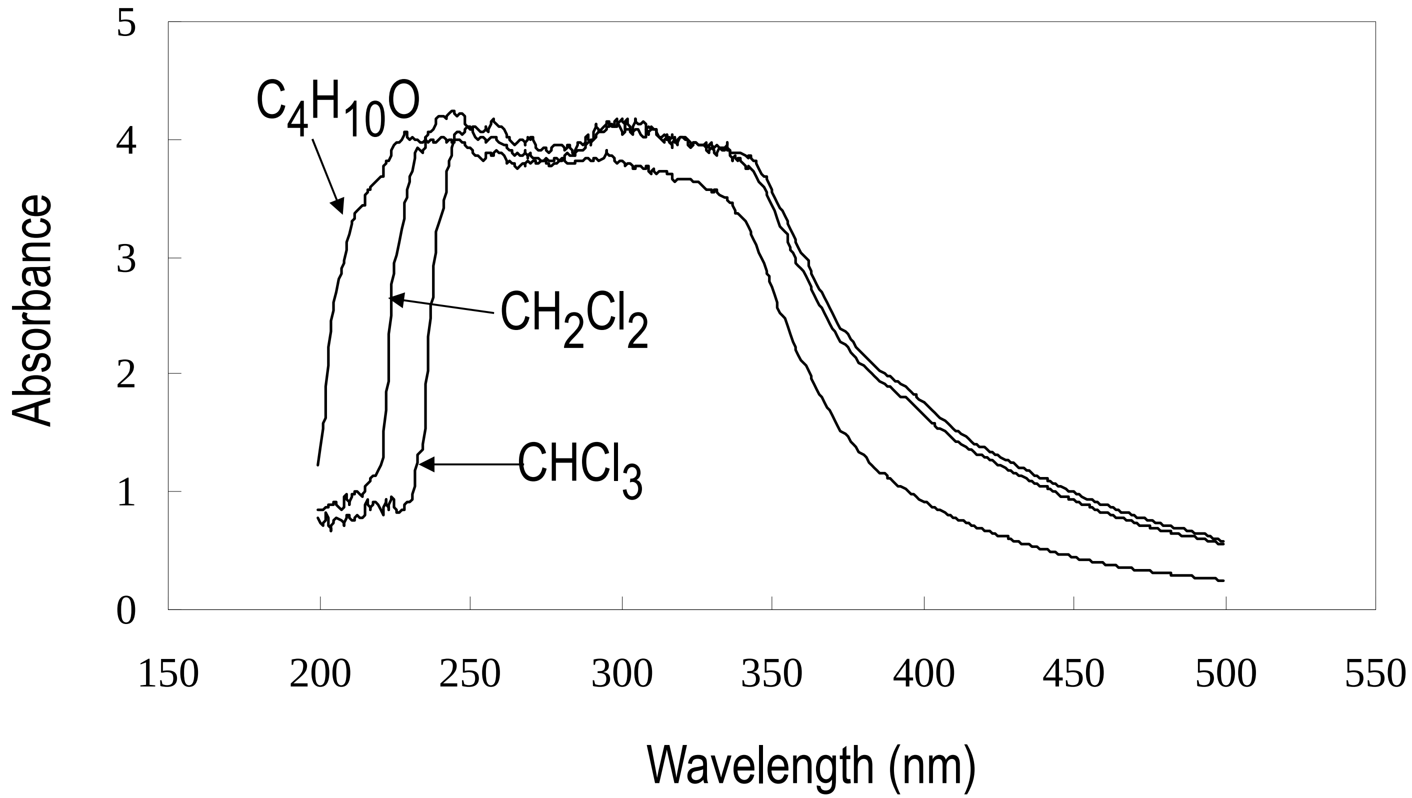


(Conditions: 125g of cattle manure, 500g of water, 0.5 mol of NaOH, residence time of 15 min, and 0 psig initial pressure of CO)

# Effects of solvents on heating values of bio-oil

| Bio-oil | Heating value ( MJ/kg) | Standard derivation |
|---|---|---|
| Bio-oil (extracted by $CH_2Cl_2$) | 36.08 | 2.06 |
| Bio-oil (extracted by $CHCl_3$) | 35.55 | 0.99 |
| Bio-oil (extracted by $C_4H_{10}O$) | 36.56 | 0.18 |
| Cattle manure | 15.2 | 0.73 |

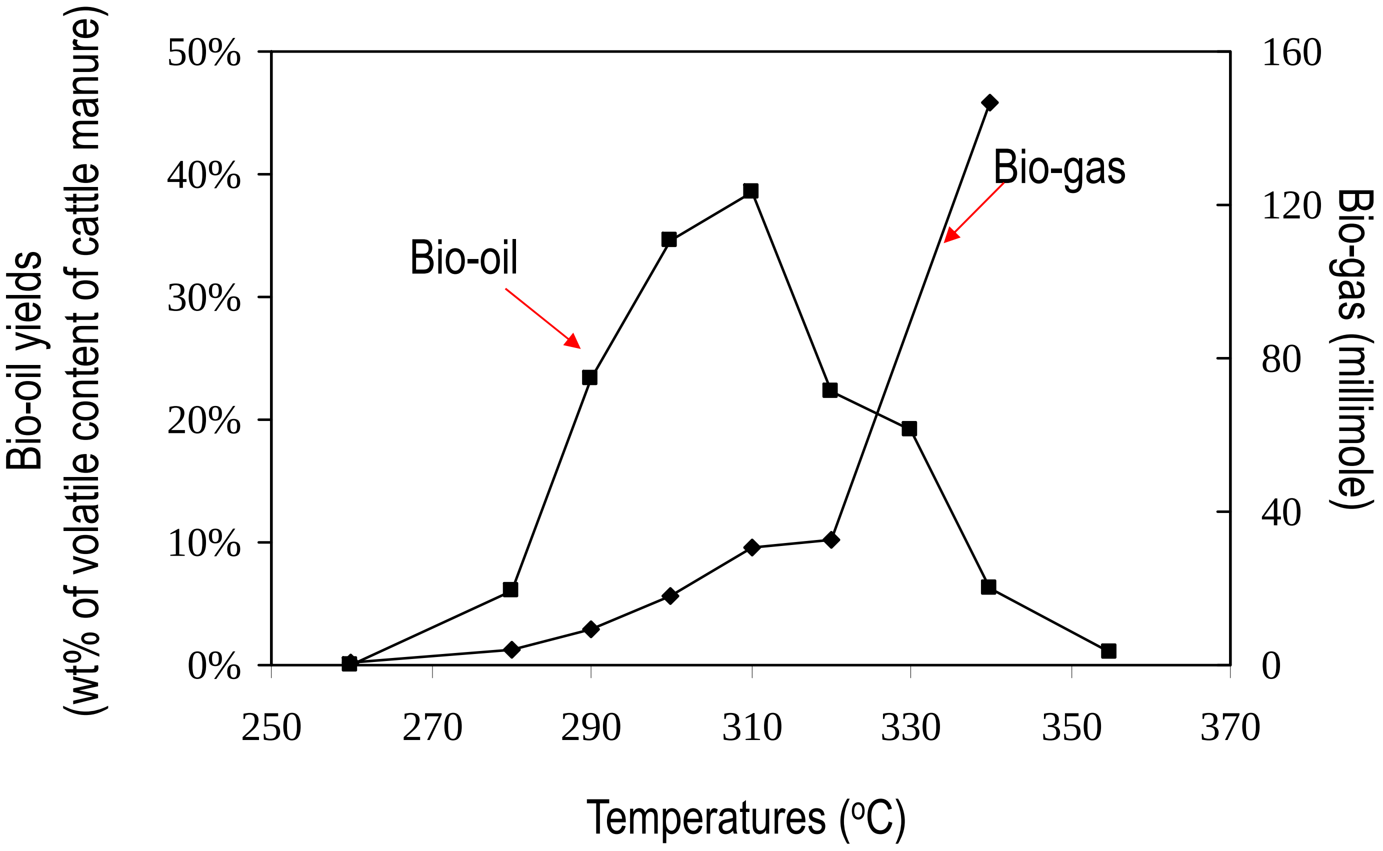
# Effects of solvents on structures of bio-oil



UV-VIS analysis spectra of bio-oil extracted by different solvents

(Conditions: 125g of cattle manure, 500mL of water, 6g of NaOH, process gas of 0 psig of CO, and residence time of 15 min)

# Effects of temperatures on bio-oil/bio-gas yields



(Conditions: 125g of cattle manure, 500g of water, 0.5 mol of NaOH, residence time of 15 min, and 0 psig initial pressure of $N_2$)

# Effects of pressures on bio-oil yields

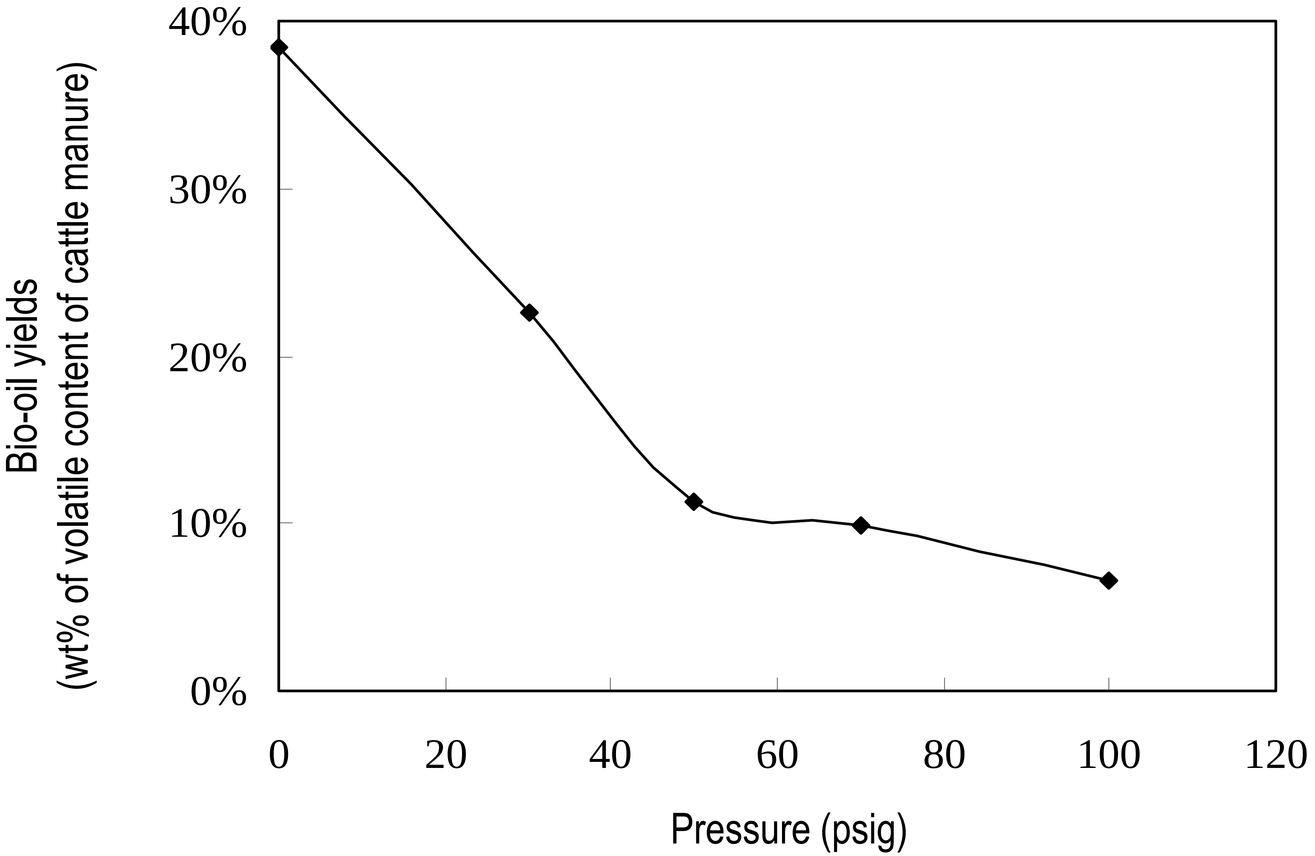


Figure 5. Effect of initial conversion pressure on biooil yield

(Conditions: 125 g of cattle manure, 500 g of water, 0.5 mol of NaOH, temperature of 310 °C, residence time of 15 min, and process gas of N2)

# Effects of processing gases on bio-oil yields

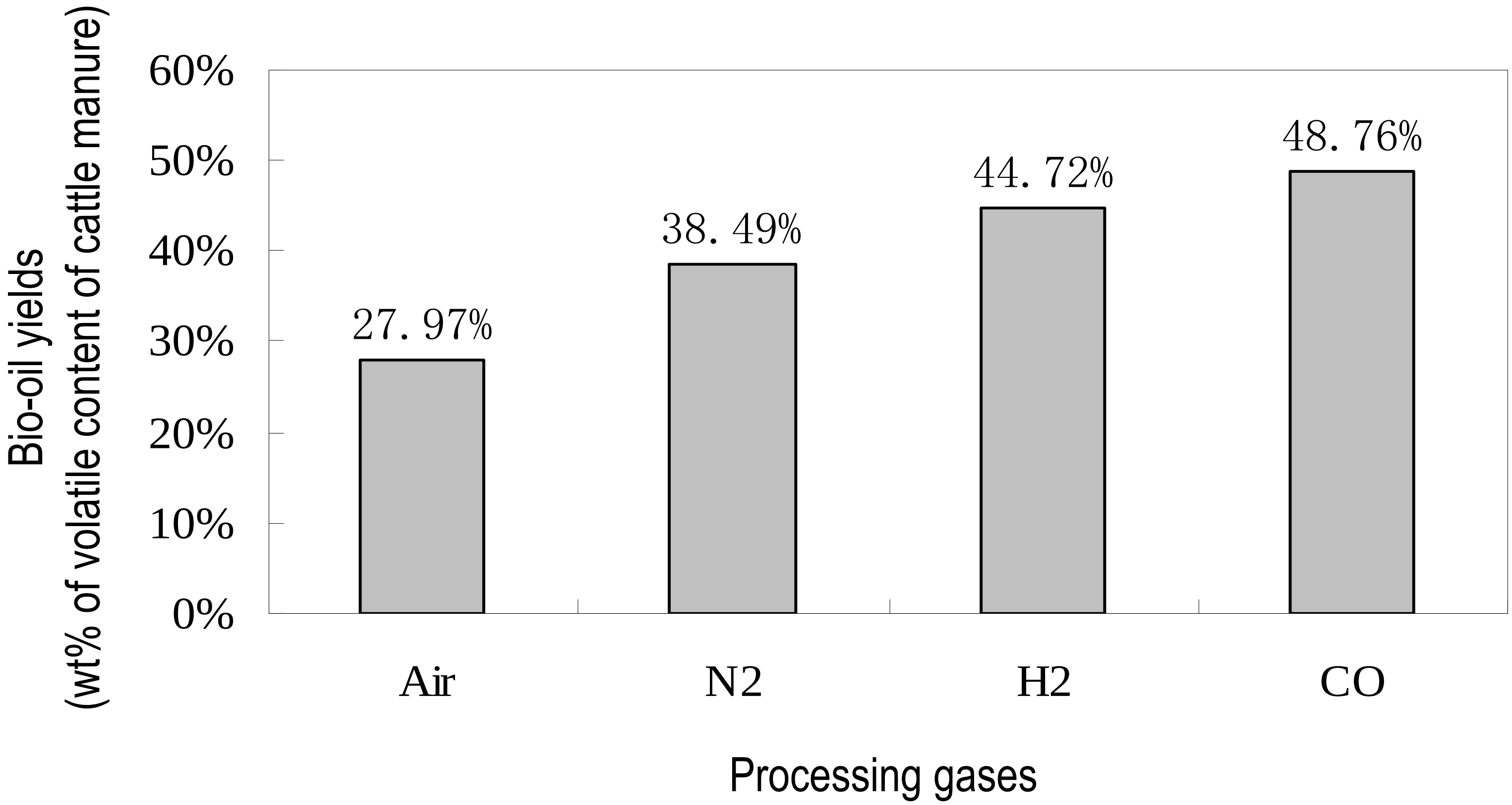


Figure 6. Effect of process gasese on biooil yield

(Conditions: 125g of cattle manure, 500g of water, 0.5 mol of NaOH, temperature of 310 °C, and 0 psig process gas)

# Effects of mass ratios of cattle manure to water on bio-oil yields

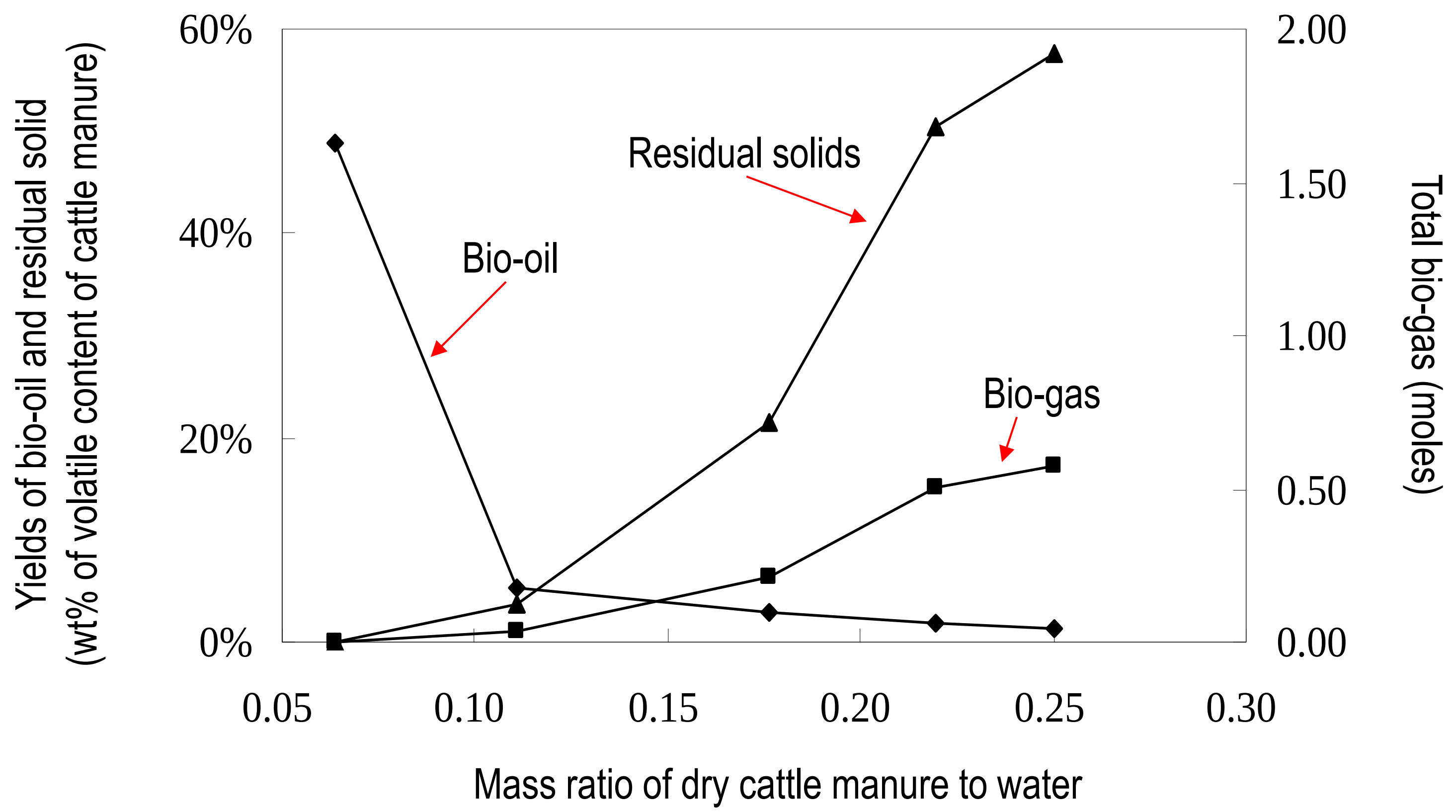
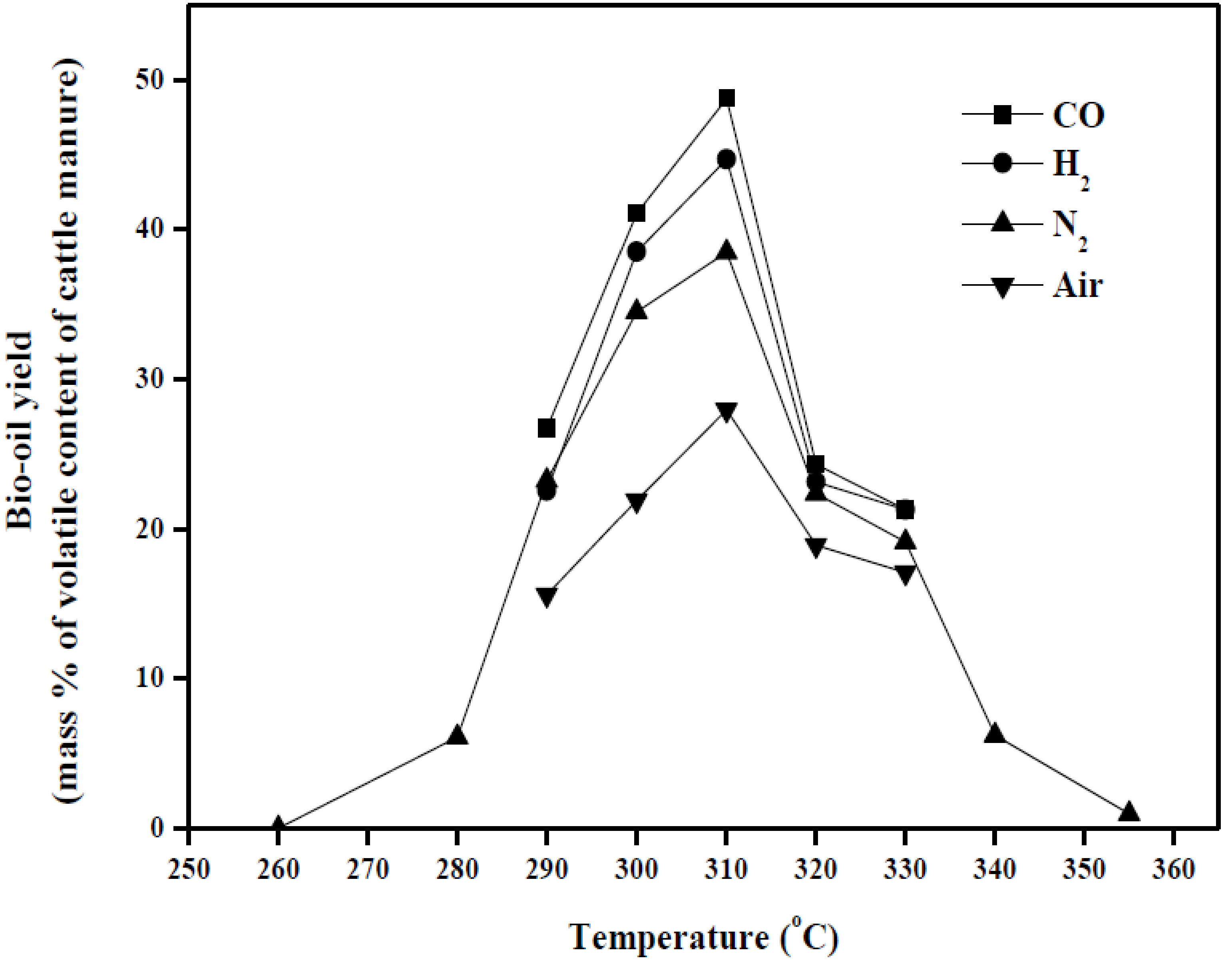


Figure 7. Effect of cattle manure to water mass ratios on bio-oil yields

(Conditions: T= 310 $^{o}$C, 0.5 mol of NaOH, residence time of 15 min,

and 0 psig initial pressure of CO)

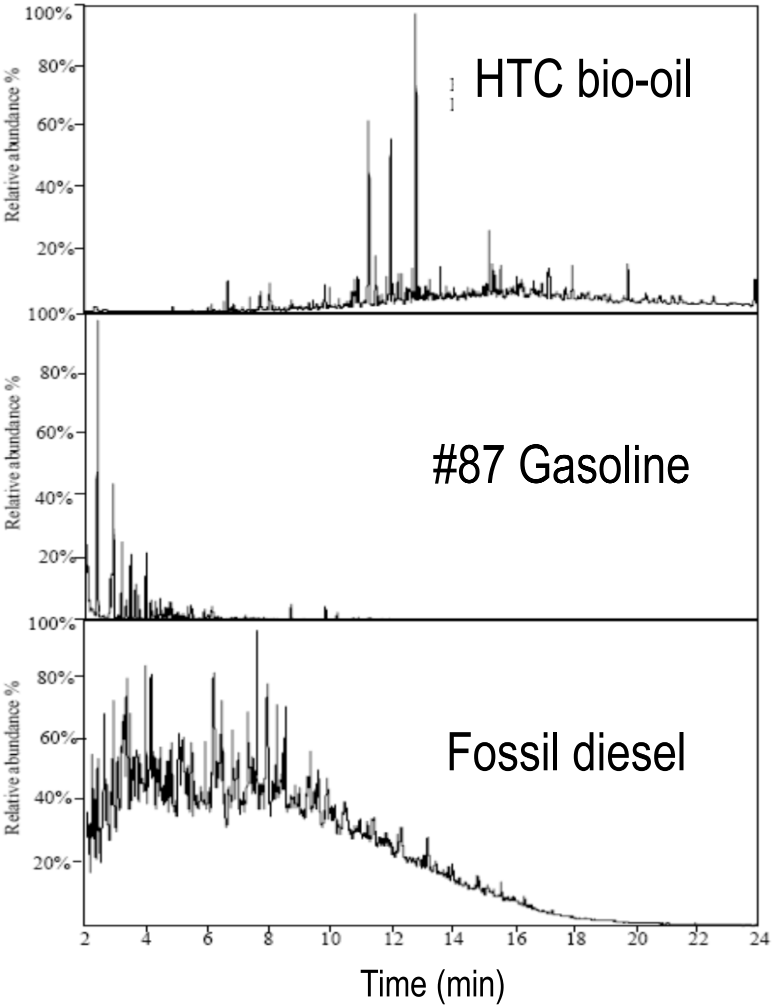
# Effects of processing gas



# High heating values of bio-oils

| **Energy types** | **Heating value( MJ/kg)** |
|---|---|
| Bio-oil from HTC | |
| 290 $^{o}$C | 35.07 |
| 300 $^{o}$C | 36.10 |
| 310 $^{o}$C | 35.74 |
| 325 $^{o}$C | 34.28 |
| Bio-ethanol | 29.8 |
| Coal | 32.5 |
| Gasohol E85 | 33.1 |
| Bio-diesel | 41 |

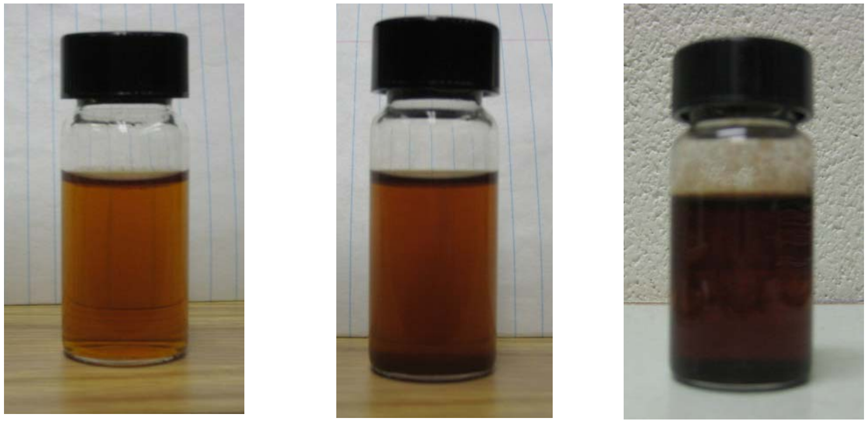
# Bio-oil from cattle manure: Comparison with petro liquid fuels



GC analysis of HTC bio-oil and fossil liquid fuels

- The main components of HTC bio-oil were carboxylic acids, aldehydes, and phenol derivatives.
- The main components of petroleum are alkanes.

# Bio-oil from cattle manure: Stability



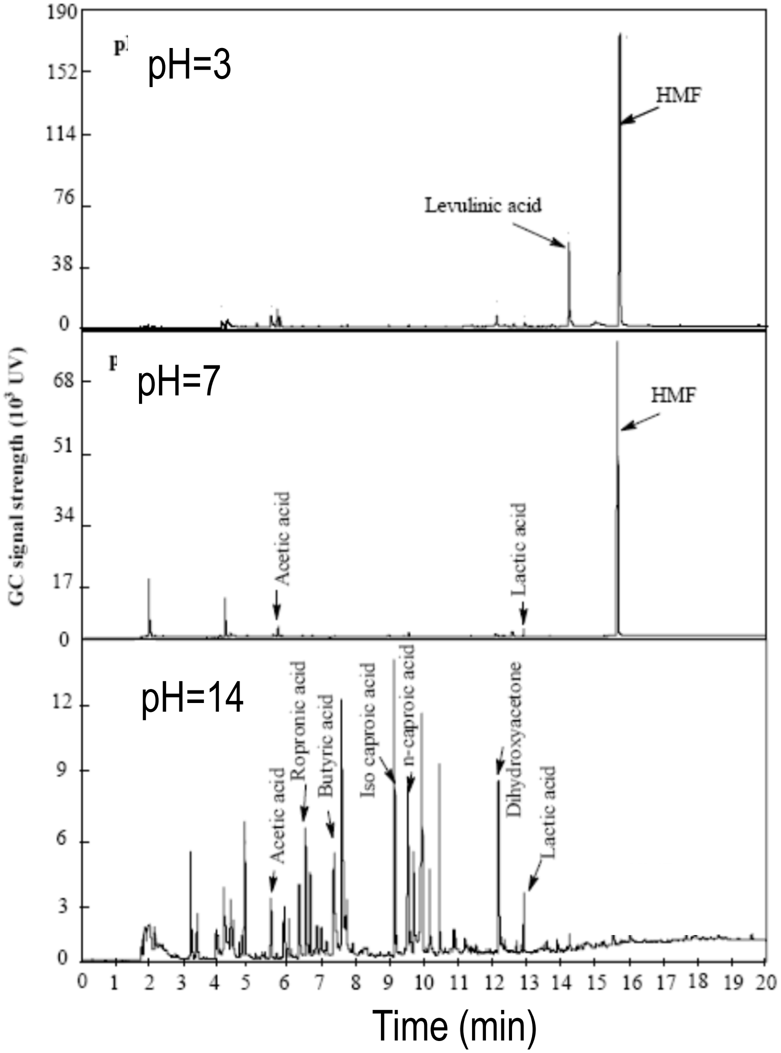
Fresh bio-oil 1 day 1 week

(It was stored at room temperature. HTC bio-oil was produced from cattle manure)

- The color of HTC bio-oil became darker with time.
- More residual solids were formed over time.
- During storage, the concentrations of aromatic chemicals and phenol derivatives decreased, while aldehydes and ketones increased.

# Hydrothermal Conversion of Cellulose to Biooil

# Bio-oil from cellulose

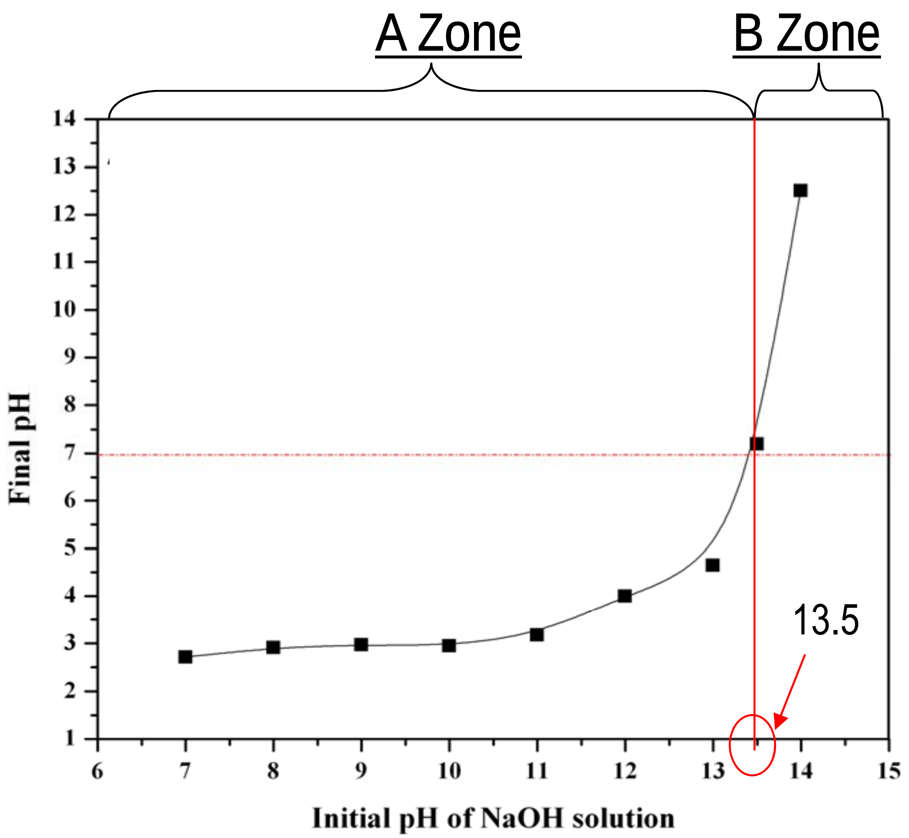


GC analysis of HTC bio-oils produced from cellulose at pH=3, 7 and 14

- No alkanes were detected in HTC bio-oil from cellulose.
- The compositions of HTC bio-oils varied with the initial pH levels of aqueous reaction media.
  - At pH<7: HMF and levulinic acid
  - At pH=7: HMF, acetic acid and lactic acid
  - At pH>7: Carboxylic acids

# pH value changes vs. initial pH level

- Reaction pathways of HTC changed during alkaline HTC



Comparison of initial and final pH levels
of alkaline HTC of cellulose to bio-oil

**A**

Cellulose
↓
Carboxylic acids
↓ Weak alkaline solutions
Final pH<7
↓
Bio-oil:
HMF+
carboxylic acids

**B**

Cellulose
↓
Carboxylic acids
↓ Strong alkaline solutions
Final pH>7
↓
Bio-oil:
carboxylic acids

# Hydrothermal Conversion of Cellulose, Glucose to Alkanes

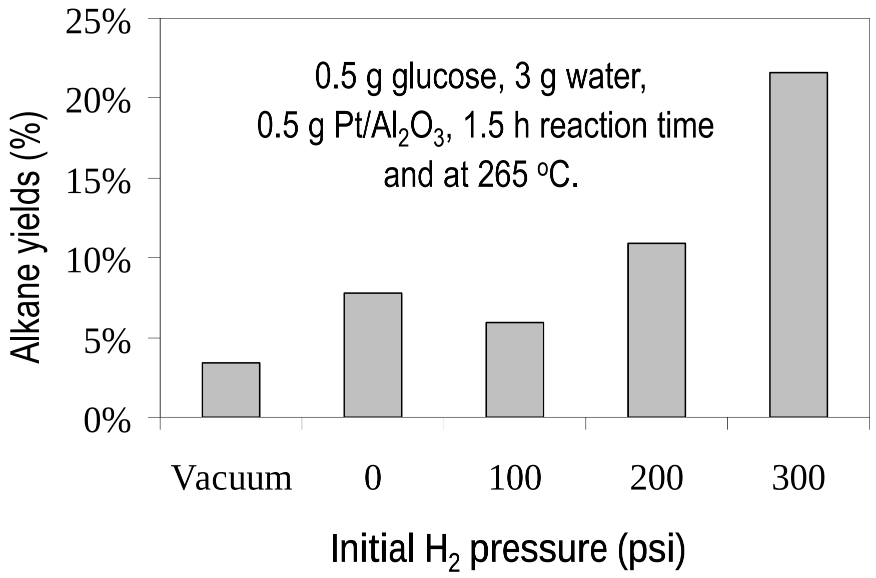
# Motivation: Previous bio-oil from cattle manure or cellulose is not "oil"

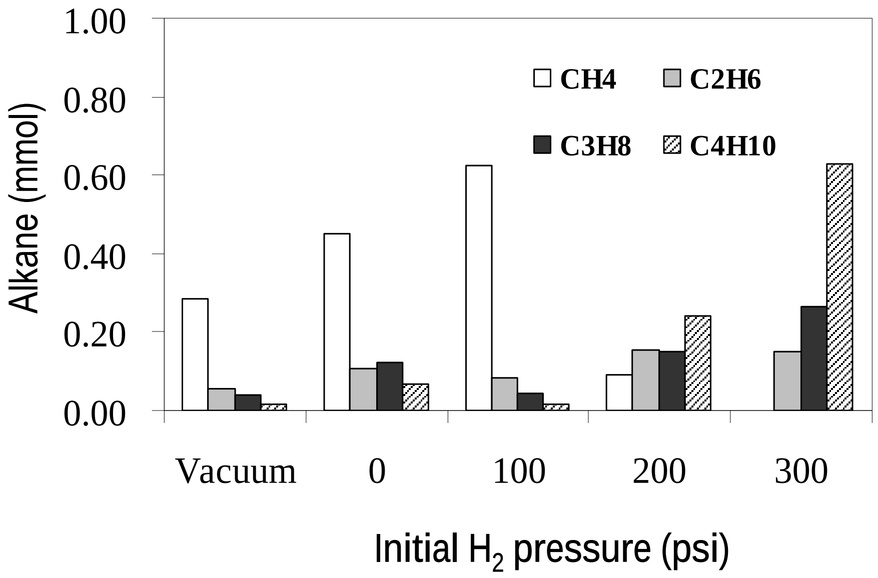
| | HTC bio-oil | Catalytic HTC bio-oil |
|---|---|---|
| Compositions | Acids, aldehyes,<br>aromatic chemicals | Alkanes<br>(Petroleum) |
| Chemical stability | Unstable | Stable |
| Separation | Organic solvent extraction | Voluntary separation from aqueous solutions |
| Use as a liquid fuel | Upgrading needed | Directly used by car engine |

- Need to improve the quality of HTC bio-oil by catalytic HTC

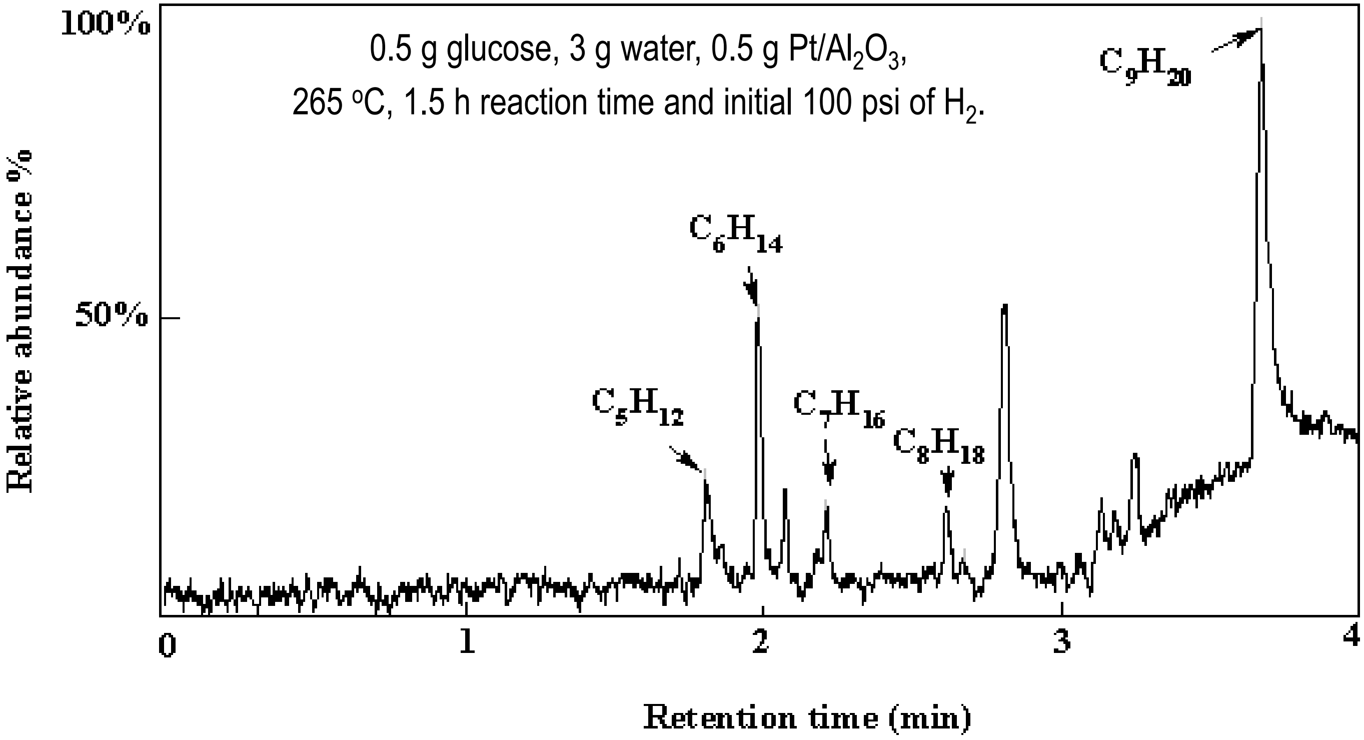
# Alkanes from CHTC of glucose with hydrogen

- Alkane yields increased with increasing $H_2$ pressure.
- More heavy gaseous alkanes ($C_3H_8$, $C_4H_{10}$) were produced with higher $H_2$ pressure.
- The chemical composition was the same as that of liquefied petroleum gas (LPG)


0.5 g glucose, 3 g water, 0.5 g $Pt/Al_2O_3$, 1.5 h reaction time and at 265 °C.



- $C_{5\text{-}9}$ liquid alkanes were detected in liquid products



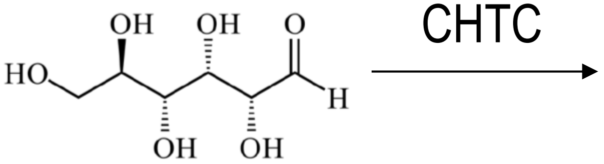
0.5 g glucose, 3 g water, 0.5 g $Pt/Al_2O_3$,
265 $^oC$, 1.5 h reaction time and initial 100 psi of $H_2$.

GC analysis of $C_{5\text{-}9}$ alkanes in liquid phase

*But, much more $C_{1\text{-}4}$ alkanes were formed than $C_{5\text{-}9}$ alkanes.*

# Alkanes from CHTC of glucose (cont…)

- Problems with CHTC of glucose to alkanes
- Few liquid alkanes were formed from glucose.



CHTC

Gaseous alkanes (C< 5)

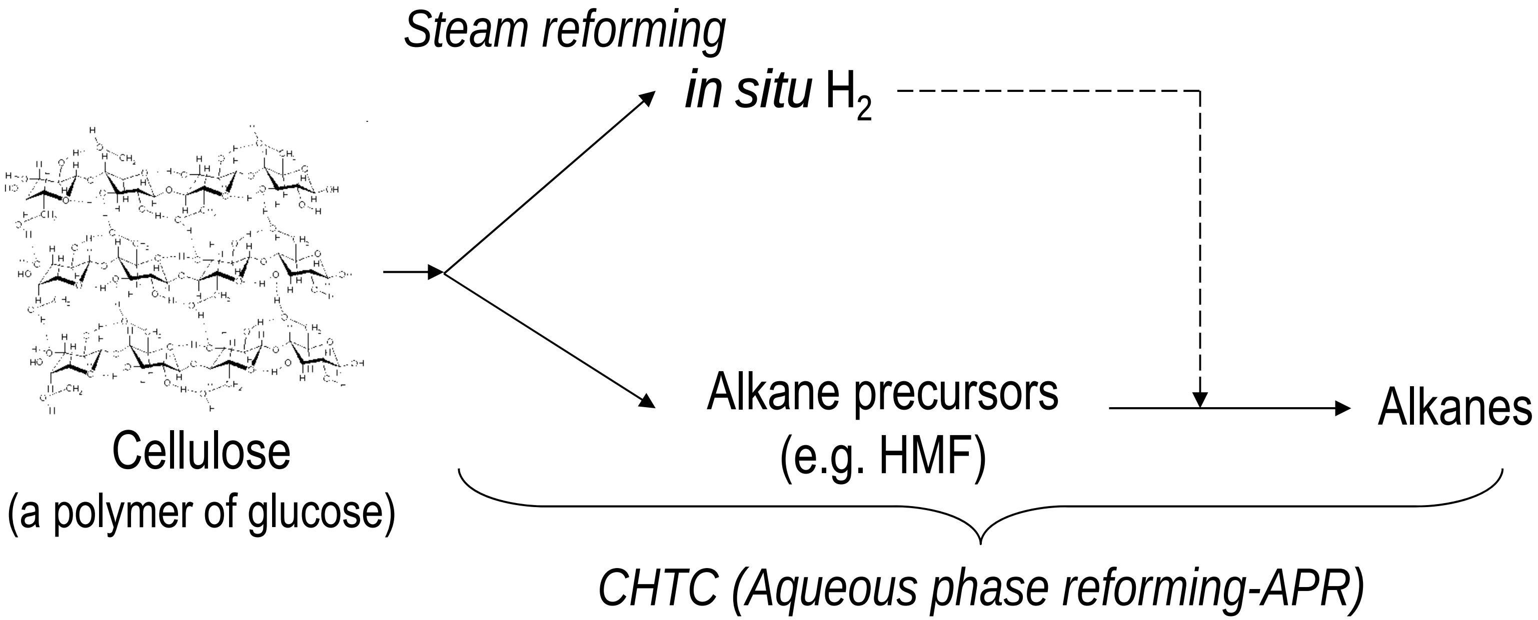
Glucose (C6)

- External $H_2$ was required for CHTC.

$H_2$ is required for hydrogenation reaction

# Alkanes from CHTC of cellulose (cont.)

- A new reaction process was proposed to produce liquid alkanes from cellulose with *in situ* $H_2$



*Steam reforming*

*in situ* $H_2$

Cellulose
(a polymer of glucose)

Alkane precursors
(e.g. HMF)

Alkanes

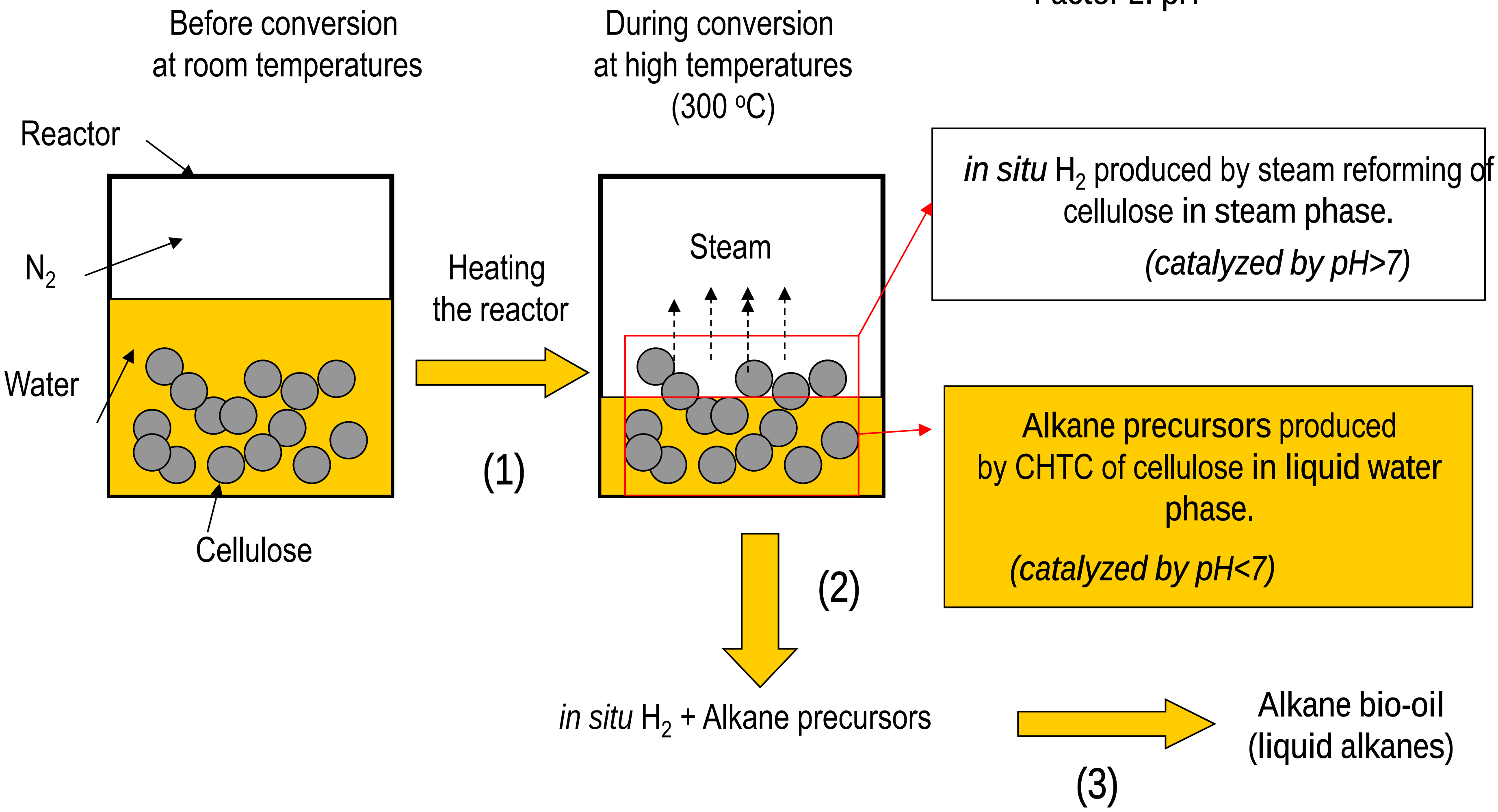
*CHTC (Aqueous phase reforming-APR)*

In-situ-$H_2$-APR

# Illustration of In-situ-$H_2$-APR process

Factor 1:v/v (water/reactor)

Factor 2: pH



Before conversion
at room temperatures

During conversion
at high temperatures
(300 $^{o}$C)

Reactor

$N_2$

Water

Cellulose

Heating
the reactor

(1)

Steam

*in situ* $H_2$ produced by steam reforming of cellulose in steam phase.

*(catalyzed by pH>7)*

Alkane precursors produced by CHTC of cellulose in liquid water phase.

*(catalyzed by pH<7)*

(2)

*in situ* $H_2$ + Alkane precursors

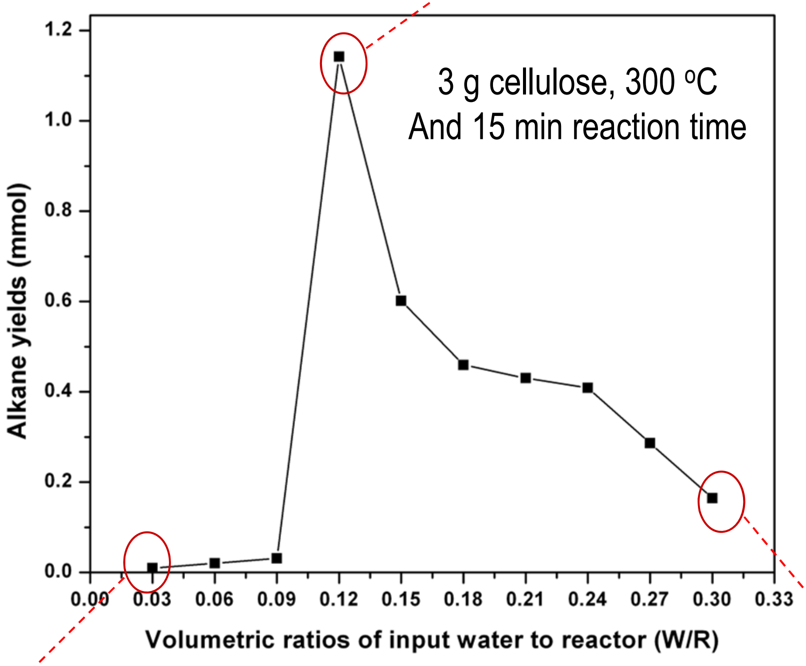
(3)

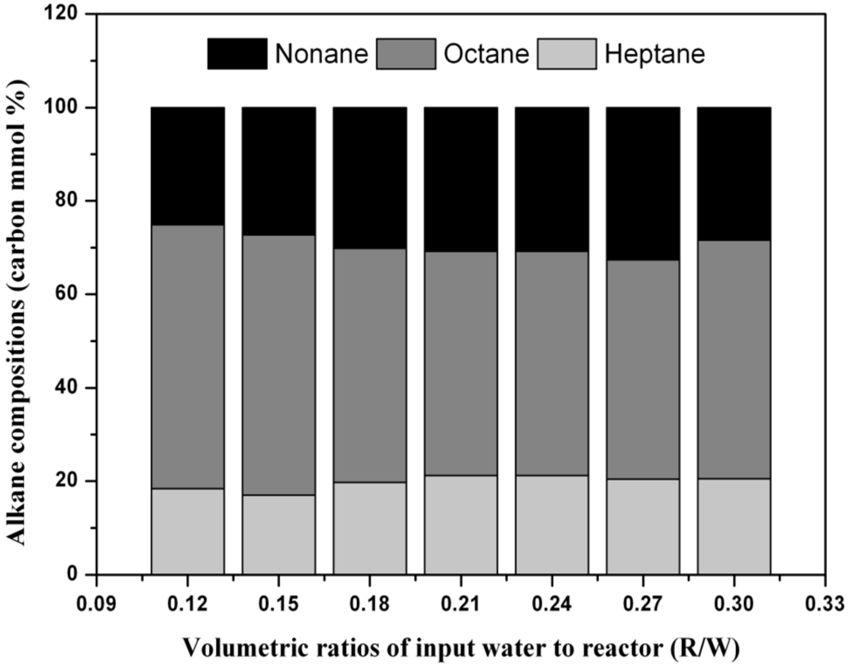
Alkane bio-oil
(liquid alkanes)

# Results: Alkanes from CHTC of cellulose

- Effects of volumetric ratios of input water to reactor
  - Too little or too much water inhibited alkane bio-oil formation.
  - The alkane bio-oil mainly consisted of nonane, octane and heptane.

*In-situ-$H_2$-APR*



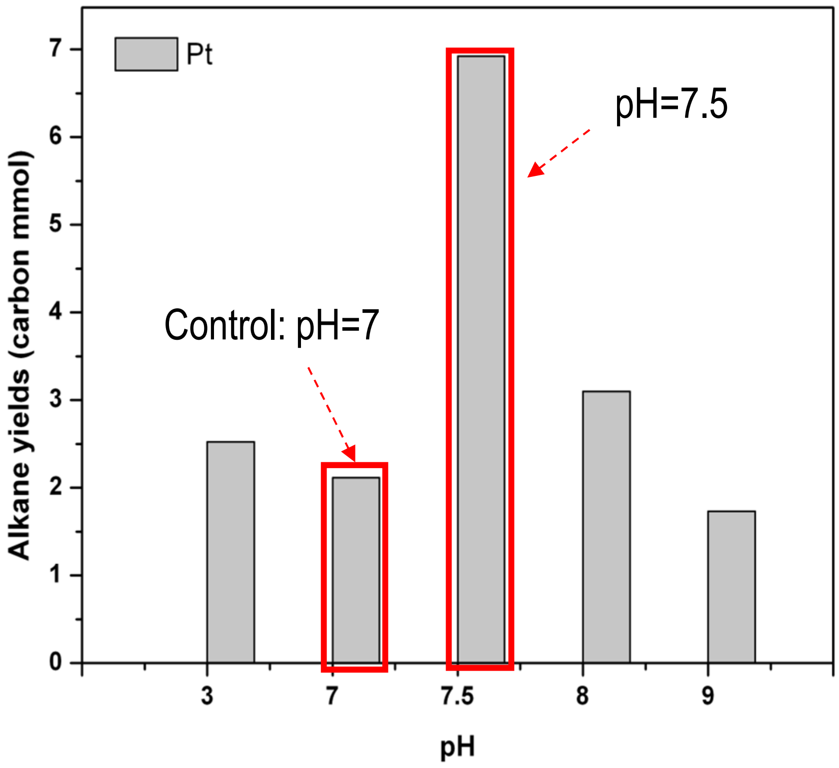


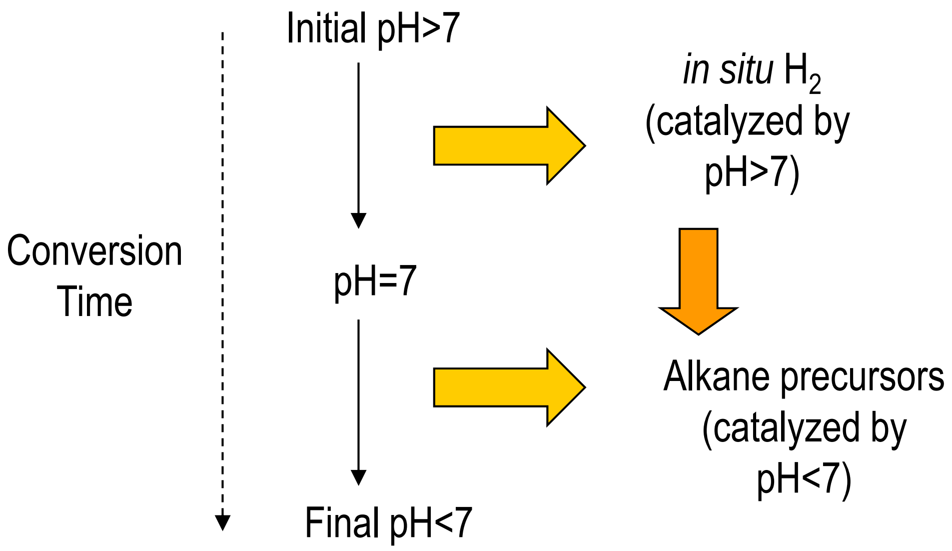
*Pyrolysis without water*

*Conventional HTC using much water*

# Results: Alkanes from CHTC of cellulose

- Effects of pH levels of aqueous reaction media
  - Alkane bio-oil yields were further increased by weak alkaline conditions.
    - pH/reaction pathway changes mainly led to this improvement.




Conversion Time

Initial pH>7

pH=7

Final pH<7

*in situ* $H_2$ (catalyzed by pH>7)

Alkane precursors (catalyzed by pH<7)

In-situ-$H_2$-APR of cellulose to alkane bio-oil under <u>weak alkaline conditions</u>

# Possible explanation to petroleum formation

- In-situ-$H_2$-APR: a possible explanation for petroleum formation

| Observations | | Petroleum formed in sea | Bio-oil formed by In-situ-$H_2$-APR |
|---|---|---|---|
| Oil | Main components | alkanes | alkanes |
| | Associated with natural gas? | Yes | Yes (syngas) |
| Environ-ment | Metals | Ni, Fe, V, Cu | Pt, Ni (catalysts) |
| | Inorganic chemicals | $SiO_2/Al_2O_3$ (the main components of earth crust) | $SiO_2/Al_2O_3$ (catalyst supports) |
| | pH | 7.5-8.4 (sea) | 7.5 (aqueous media) |
| | Steam | Geothermal heating | External heating |
| | Liquid water | Yes | Yes |

# Conclusions

1. HTC bio-oil was different from petroleum, in terms of chemical composition.
2. HTC bio-oil compositions were unstable and changed with time.
3. But, by CHTC (especially, In-situ-$H_2$-APR), alkane bio-oils were produced from glucose and cellulose. Their compositions are quite same as liquefied petroleum gas and gasoline, respectively.
4. Via catalytic HTC, therefore, a quick production of petroleum from renewable/carbon-neutral biomass would become feasible.

# Other Slides

# Biomass is Biological Material Derived from Living Organisms Recently

Absorb $CO_2$ and solar energy

Three types of biomass:

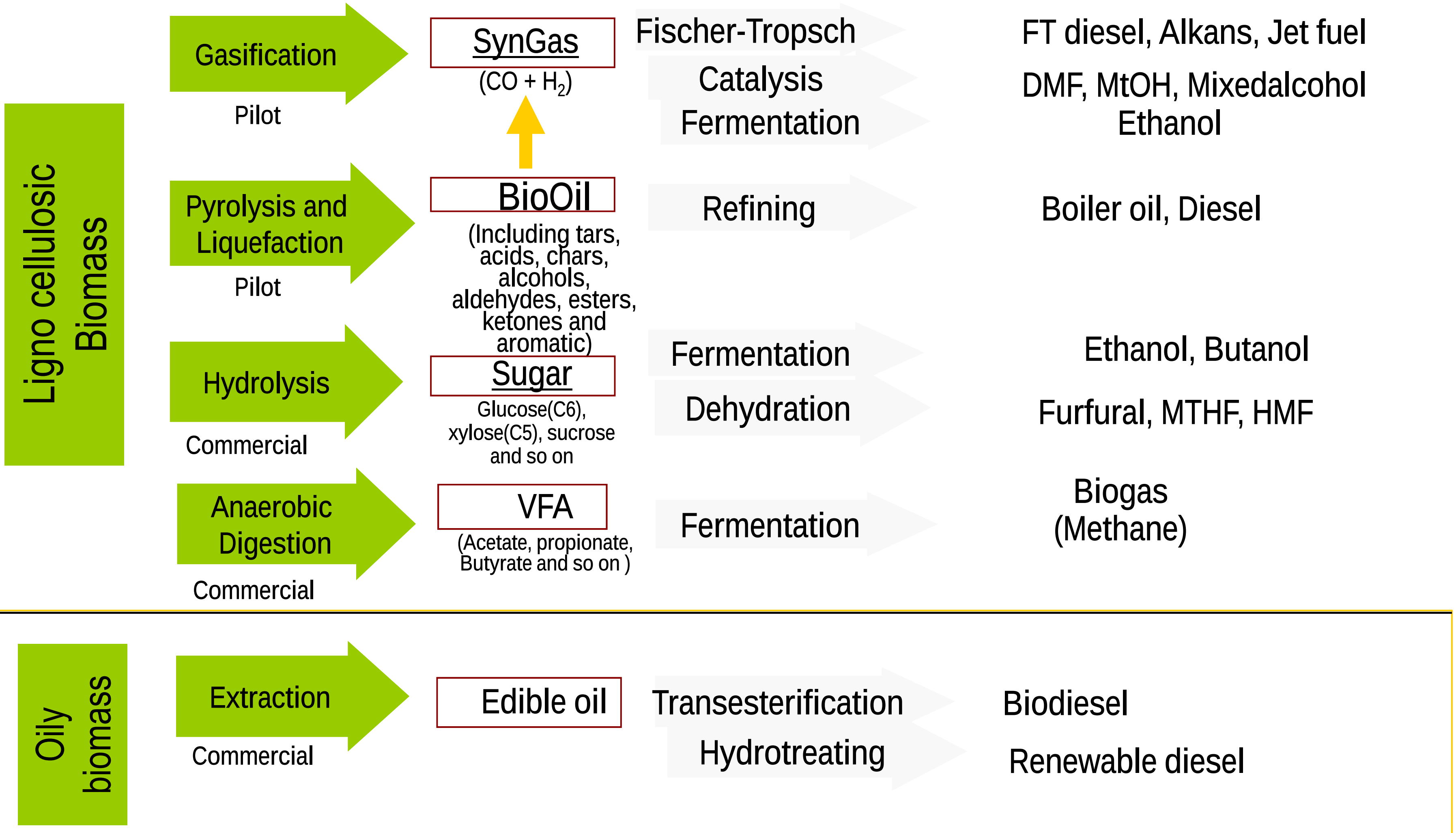
- Lignocellulosic and starch-based plants (e.g. Wood, grass, livestock manure)
- Triglyceride-producing plants: e.g. canola, soybeans, sunflower, safflower
- Algae are another source of triglycerides as well as carbonhydrates and lignin.

# Transportation Energy Needs to Remain Liquid to Fit in Existing Tanks and Be Transportable

- World has ~ 800 million vehicles, and adds 50 million vehicles per year
- Biomass is the only renewable source for renewable transportation fuel.
- Biofuel is the solution before electrical car becomes affordable and reliable.
- Biofuel may remain important since other sectors demands electricity rather than fuel.

Henry Ford originally designed the Ford Model T to run completely on ethanol. But then crude oil became more cheaply available.

# Platforms for Biofuel Production[3]



| | | | | | |
|---|---|---|---|---|---|
| Ligno cellulosic Biomass | Gasification | Pilot | SynGas<br>(CO + $H_2$) | Fischer-Tropsch<br>Catalysis<br>Fermentation | FT diesel, Alkans, Jet fuel<br>DMF, MtOH, Mixedalcohol<br>Ethanol |
| | Pyrolysis and Liquefaction | Pilot | BioOil<br>(Including tars, acids, chars, alcohols, aldehydes, esters, ketones and aromatic) | Refining | Boiler oil, Diesel |
| | Hydrolysis | Commercial | Sugar<br>Glucose(C6), xylose(C5), sucrose and so on | Fermentation<br>Dehydration | Ethanol, Butanol<br>Furfural, MTHF, HMF |
| | Anaerobic Digestion | Commercial | VFA<br>(Acetate, propionate, Butyrate and so on ) | Fermentation | Biogas (Methane) |
| Oily biomass | Extraction | Commercial | Edible oil | Transesterification<br>Hydrotreating | Biodiesel<br>Renewable diesel |

- Syngas and Sugar platform : two actively researched field for the liquid fuel

Canadian Renewable Fuels Association (CRFA)

# Canada

# Challenges to existing biofuels

- ❑ Mostly from edible biomass
- ❑ High cost: 90% of $$$ goes to separation
- ❑ Mixed with petroleum gasoline

| Bio-oil | Feedstock | Pretreatment | Use as liquid fuel |
|---|---|---|---|
| Bio-ethanol | Food crops<br>(e.g. Corn, wheat) | Not required | 1. Needing to be mixed with petroleum before use<br>2. Not used in cold weather (low vapour pressure of ethanol) |
| Bio-diesel | Food crops<br>(e.g. Canola oil) | Predrying biomass | 1. Not used in cold weather (gelling at low temperatures < -10 °C) |

# New Generation Biofuels:
# Cellulosic Feedstock…

Switchgrass

Wheat Straw

Hybrid Poplar

Corn Stalks

# Sustainable Production of Biofuels: An Integrated Biomass Production System