

Abstract

Lignin, cellulose and hemicelluloses from biomass have been shown to break down into sustainable fuel products when subjected to extreme reaction conditions. However, factors such as energy costs, char generation, and low yields hinder the mainstream use of biofuels. This project investigated the effects of catalytic molten salts on biomass feedstocks in producing gaseous and liquid fuels using the mechanistic chemical pathways of gasification, pyrolysis, thermal depolymerization, hydrolysis and transesterification. Reaction variables such as flow rates, temperature, pressure, vessel type, reagent type, and time were investigated. Gaseous and liquid products were purified and qualitative observation, NMR and GC data were collected for positive product identification. Optimization techniques such as reducing char buildup by protein digestion, running semi-batch conditions, and the use of microwave reactors were all investigated to increase the efficacy of the system. Specific reaction conditions for gasification, pyrolysis and transesterification resulting in the desirable production of syngases and biodiesel-like products were identified. Recommendations were made for more specific identification of oily products, improved reactor design, and conditions for depolymerization of plastics.

Background

Energy has been a controversial topic in science, politics and everyday life during the modern age. Concerns of depleting fossil fuel reserves, increasing greenhouse gas production and increasing pollution have led to renewed interest in investigating alternative sources of fuel. Energy demands in 2005 were approximately 210 million oil-equivalent barrels per day. Over the next few years, this is expected to grow to over 300 oil-equivalent barrels per day, an increase of approximately 35%.

The world is currently facing the following energy related issues which must be addressed:

- Depleting oil resources and rising energy costs in price per barrel of oil (currently \$84 per barrel).
- The majority of solid waste generation is not being recycled contributing to pollution. Of the 249.6 million tons of solid waste generated in 2008 in the United States, only 82.9 million tons were recycled (33%).
- An increase in Greenhouse Gas, NO_x, and SO₂ emissions. Although technologies such as adsorption and gas scrubbers are beginning to reduce harmful effects of these emissions, there is still a net increase of emissions yearly due to rising energy demands.
- High costs of generating renewable energy (more expensive than oil). Poor conversion efficiencies, energy loss in transfer, char accumulation and catalyst cost remain barriers of low cost.

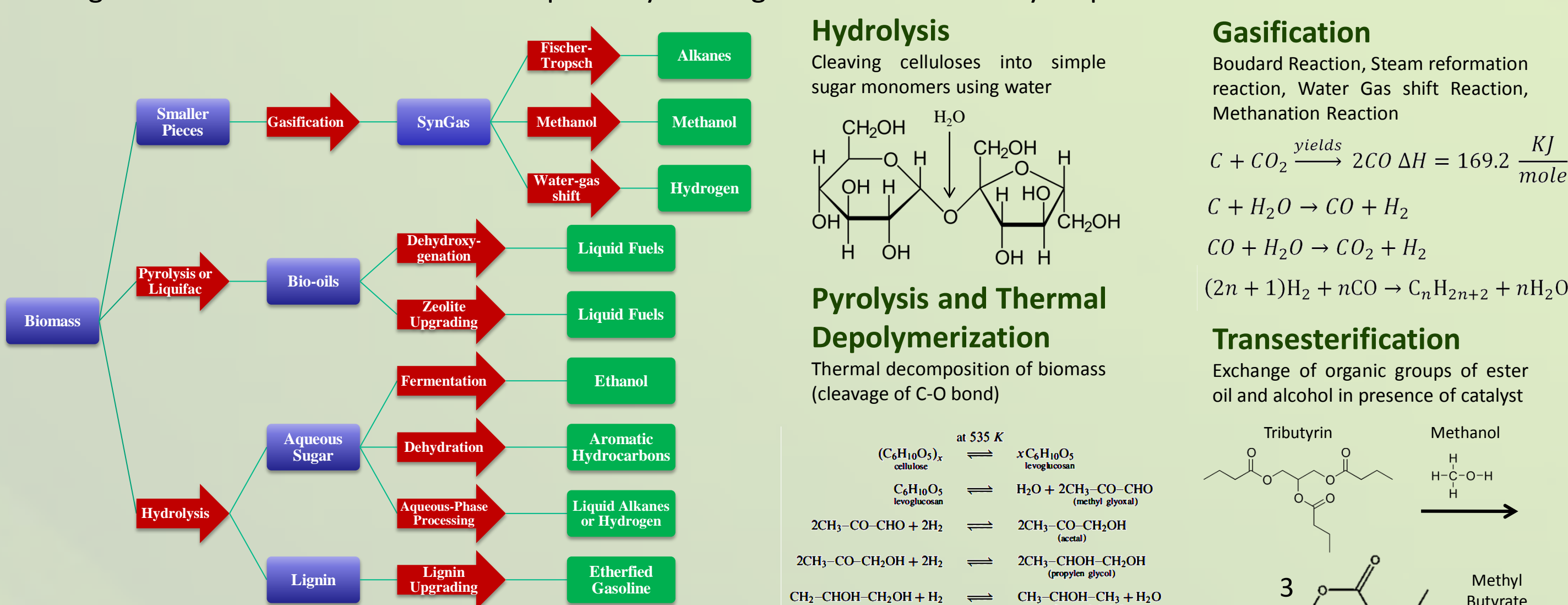
These issues all contribute to an unsustainable model for energy production and use for the world. Alternate renewable methods of energy production have been extensively researched over the past few decades in an effort to alleviate these issues to ensure a sustainable future. However, these methods must still be refined further to match or exceed the high efficiency, low cost, and high yield of fossil fuels.

Introduction

Production of energy from biomass has the potential to alleviate some of the energy demanded by industry and individuals. Advantages of biomass conversion into energy include:

- High feedstock availability and variability. Existing waste products may be used as feedstocks.
- High product variability. Target syngas or liquid fuel products are produced based on reaction conditions.
- Carbon neutrality and low pollution. All carbon released in burning biofuels is fixed in plants.

The figure below shows the mechanistic pathways through which biofuels may be produced from biomass.



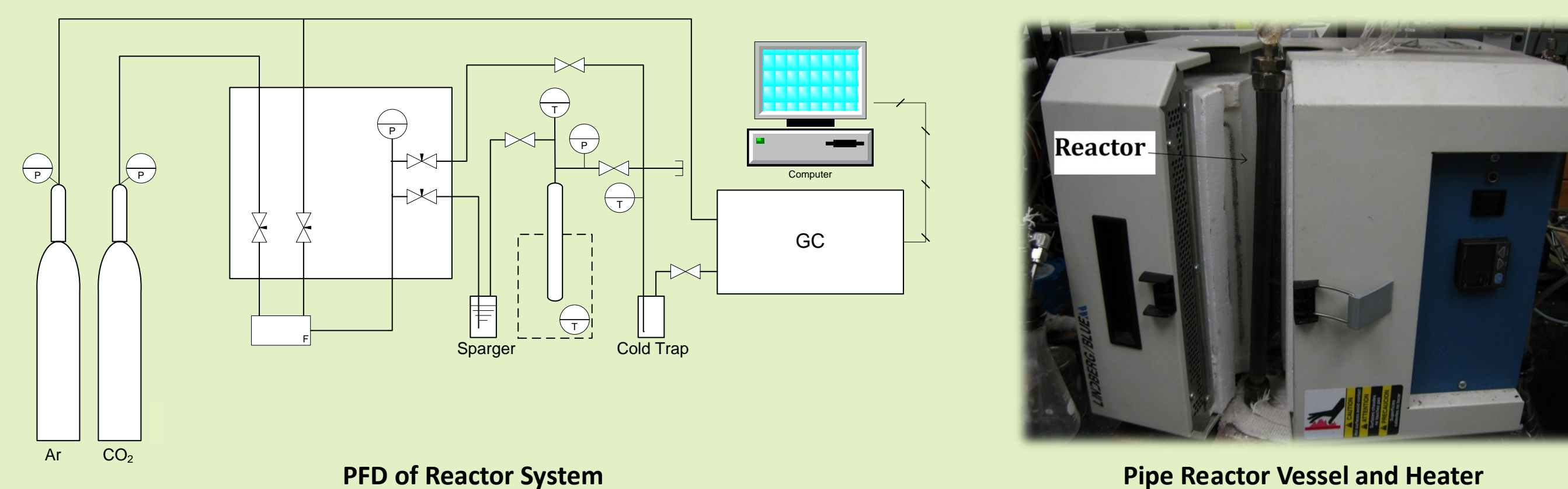
Molten Salts are inorganic ionic salts which melt above temperatures of 100°C. Eutectics of these salts have been shown to increase the reactivity of reactions through catalysis in biomass conversion to syngas. Molten salts function as strong oxidizing agents, corroding agents, and agents of catalysis. Molten salts are ionic and small enough to cleave the most hindered glycosidic bonds allowing acid and base catalyzed reactions to proceed with a 5X higher activity over solid oxide catalysts in gasification reactions.

It has been proposed that the addition of molten salt catalysts may increase the activity of pyrolysis, thermal depolymerization, hydrolysis and transesterification reactions in producing liquid fuel products.

Objectives

- Modify existing reactor system for semi-batch operation to determine effect of time on syngas production
- Determine the effects of varying flow rate, flow gas type, temperature, pressure, reagent type, biomass feedstock type and amount and type of molten salt
 - ❖ Syngas composition and concentration of gasification reactions
 - ❖ Liquid product production, composition and concentration in hydrolysis, pyrolysis, transesterification and thermal depolymerization pathways
- Investigate the minimization of char due to lignin through enzymatic biocatalysis using Proteinase K
- Investigate effect of alternative reactor designs and modifications such as Microwave Reactors and spargers
- Use tributyrin feedstock to determine if transesterification and hydrolysis are occurring at high temperatures
- Determine specific conditions at which most desirable syngas and liquid products are produced

Methodology



General Reaction Procedure

- System Construction
- Gas Controller Calibration
- GC Column Calibration and Operating Specifications
- Running reactions
 - ❖ Determine reaction specifications
 - ❖ Clean reactor, leak test, and refill sparger vessel
 - ❖ Charge reactor with salts, reagents and biomass
 - ❖ Secure reaction vessel and flood free of air
 - ❖ Set gas type, flow rate and reactor temperature
 - ❖ Turn on heater, begin reaction and take GC samples throughout the duration of reaction
 - ❖ Remove and separate solid and liquid products
- Analyze gas product composition and concentration
- Purify liquid samples
 - ❖ Add Ethyl Acetate solvent
 - ❖ Separate organic phase
 - ❖ Rotoevaporate samples
 - ❖ Filter sample using 0.45 μm filters
- Analyze liquid products using GC and NMR and compare against standardized control

Controls

- Gas Products
 - ❖ H₂, CO, CO₂, CH₄ retention times and gas constants determined in SRI 8610C GC with 60/80 carboxen 1000 packing 1/8" 15 foot column
- Liquid Products
 - ❖ Ethyl Acetate, Methanol, Vegetable Oil, Tributyrin (oil), Methyl Butyrate, Butyric Acid and Glycerol retention times and spectra for GC and NMR determined

Lignin and Protein Digestion

- 4g crushed lima beans in 4 mL volume of 1% Triton X-100 and 0.5% SDS
- 1 mg >30 units/mg reconstituted Proteinase K in water with Ca²⁺
- Incubate at 37°C for 3 hours or 48 hours while digestion occurs
- Deactivate with EDTA
- Prepare reaction using General Reaction Procedure
- Test gasification ability, liquid product formation, char reduction

Bench Top Trials Performed Salt Eutectic Furnace Tests

Reactions

Reaction Conditions for Gasification Trials							
Trial No.	Paper (grams)	Salt Used	Salt (grams)	Water (mL)	Temperature (C)	Time (Hours)	Gas Flow (mL/min)
1	5	KOH	5	0	200	1.00	CO ₂ 75.00
2	5	KOH	10.5	0	500	1.00	CO ₂ 12.50
3	5	Eutectic	10	0	500	1.00	CO ₂ 10.00
4	5	Eutectic	10	0	500	2.00	CO ₂ 10.00
5	5	Eutectic	10	0	500	8.92	CO ₂ 10.00
6	5	KOH	10	0	500	9.00	CO ₂ 10.00
7	5	Eutectic	10	0	500	8.92	CO ₂ 10.00
8	5	KOH	10	Sparger	500	10.17	CO ₂ 10.00

Reaction Conditions for Depolymerization of Plastics							
Trial No.	Plastic (grams)	Salt Used	Salt (grams)	Water (mL)	Temperature (C)	Time (Hours)	Gas Flooded Pressure (psi)
1	5	Eutectic	10	0.00	500.00	1.00	Ar 60.00
2	5	Eutectic	5	4.00	500.00	1.00	Ar 60.00

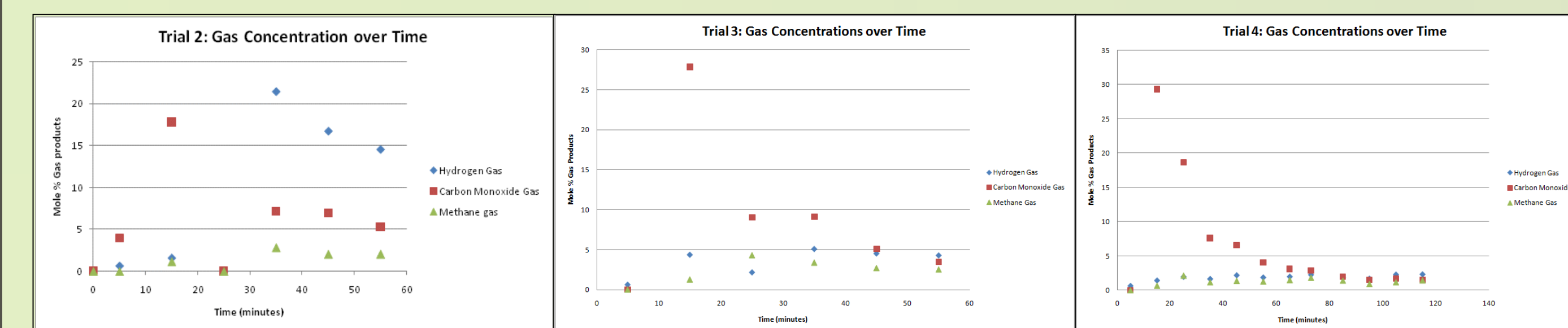
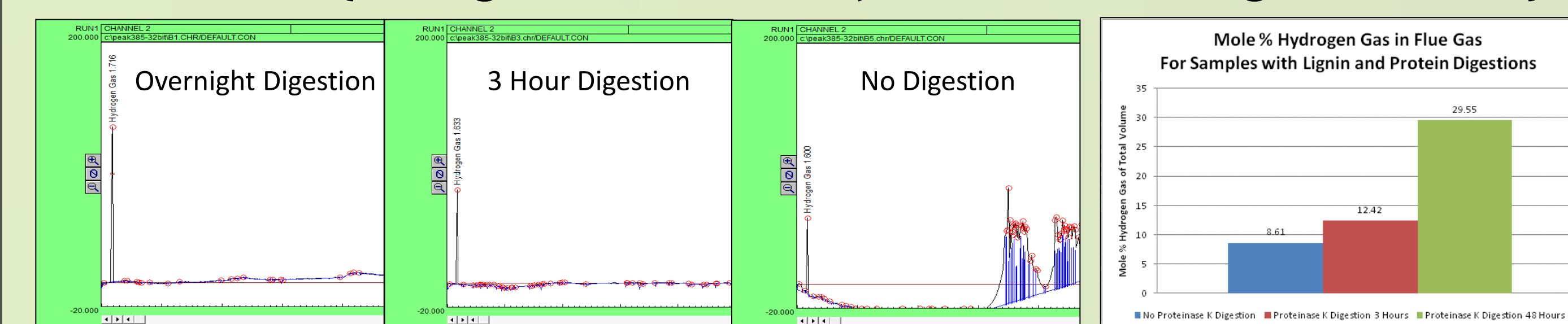
Reaction Conditions for Bench Top Biodiesel Trials							
Trial No.	Oil Used	Oil (mL)	Salt Used	Salt (grams)	Water / Methanol (mL)	Amount (mL)	Time (Hours)
1	Vegetable Oil	100	NaOH	0.35	Water	20.00	0.50
2	Vegetable Oil	100	NaOH	0.35	Methanol	20.00	0.50
3	Tributyrin	100	NaOH	0.35	Water	20.00	0.50
4	Tributyrin	10	NaOH	0.14	Methanol	10.00	0.50

Reaction Conditions for Transesterification Reactions in the Reactor								
Trial No.	Oil/Biomass Used	Salt Used	Salt (grams)	Water / Methanol (mL)	Amount (mL)	Temperature (°C)	Time (Hours)	
1	Tributyrin	4	NaOH	0.50	Water	4.00	200.00	0.50
2	Tributyrin	4	NaOH	0.50	Water	4.00	250.00	0.50
3	Tributyrin	4	NaOH	0.50	Water	4.00	300.00	0.50
4	5	Eutectic	10	0.50	Water	4.00	200.00	0.50
5	5	Eutectic	10	0.50	Water	4.00	350.00	0.50
6	5	Eutectic	10	0.50	Water	4.00	400.00	0.50
7	5	Eutectic	10	0.50	Water	4.00	500.00	0.50
8	5	Eutectic	10	0.50	Water	4.00	500.00	0.50
9	5	Eutectic	10	0.50	Water	4.00	250.00	1.00
10	5	Eutectic	10	0.50	Water	4.00	250.00	2.00
11	5	Eutectic	10	0.50	Methanol	4.00	200.00	0.50
12	5	Eutectic	10	0.50	Methanol	4.00	300.00	0.50
13	5	Eutectic	10	0.50	Methanol	10.00	300.00	0.50

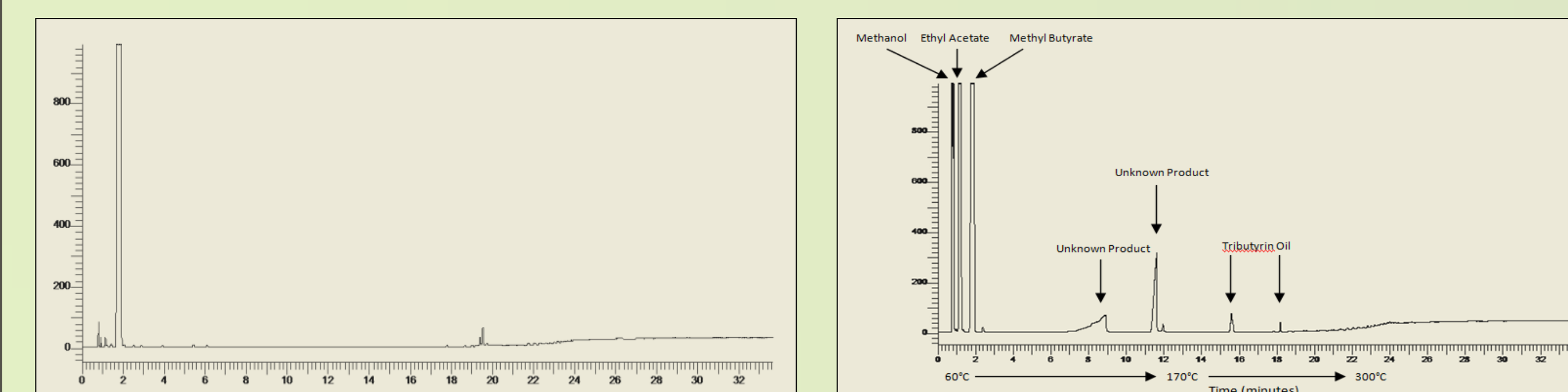
Reaction Conditions for Enzymatic Biocatalysis Prior to Changing the Reactor									
Trial No.	Digestion Time	Reaction Pathway	Gas Type	Salt Used	Salt (grams)	Water / Methanol (mL)	Temperature (°C)	Batch/Flow	
1	48 hr	Gasification	CO ₂	Eutectic	5.00	Water	3.00	500	Flow
2	48 hr	Esterification	Ar	NaOH	5.00	MeOH	3.00	300	Batch
3	3 hr	Gasification	CO ₂	Eutectic	5.00	Water	3.00	500	Flow
4	3 hr	Gasification	Ar	NaOH	5.00	MeOH	3.00	300	Batch
5	Control	Gasification	CO ₂	Eutectic	5.00	Water	3.00	500	Flow
6	Control	Esterification	Ar	NaOH	5.00	MeOH	3.00	300	Batch

Results

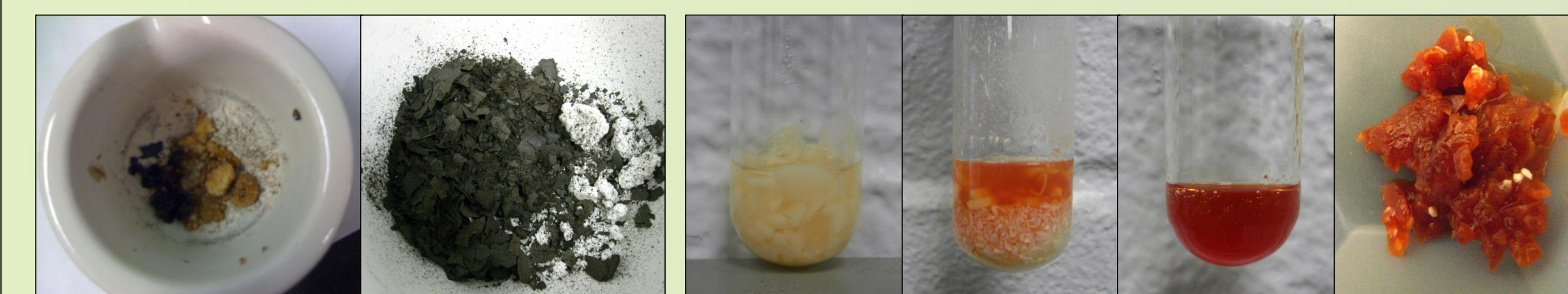
Gasification (71 GC gas identification injections made throughout 14 trials)



Liquid Identification (36 liquid products from trials in GC and NMR)



Char Breakdown and Qualitative Inspection



Conclusions

- Concentration of gasification products is highly dependent on reaction time, salt catalyst type
- Addition of water vapor by a sparger forced the water gas shift reaction
- Organic liquid products produced during gasification trials indicate that gas and liquid products may be produced simultaneously through multiple mechanistic pathways
- Hydrolysis was unsuccessful with tributyrin but produced volatile oily products when attempted with heavier oils
- Hydrolysis is highly dependent on conditions
- The transesterification mechanistic pathway was proven to occur at both high and low temperatures.
- Thermal depolymerization of plastics yielded no liquid products
- Pre-treatment with Proteinase K reduced char, increased syngas production and yielded organic volatile products
- Microwave reactor technology would need to be significantly altered for use