

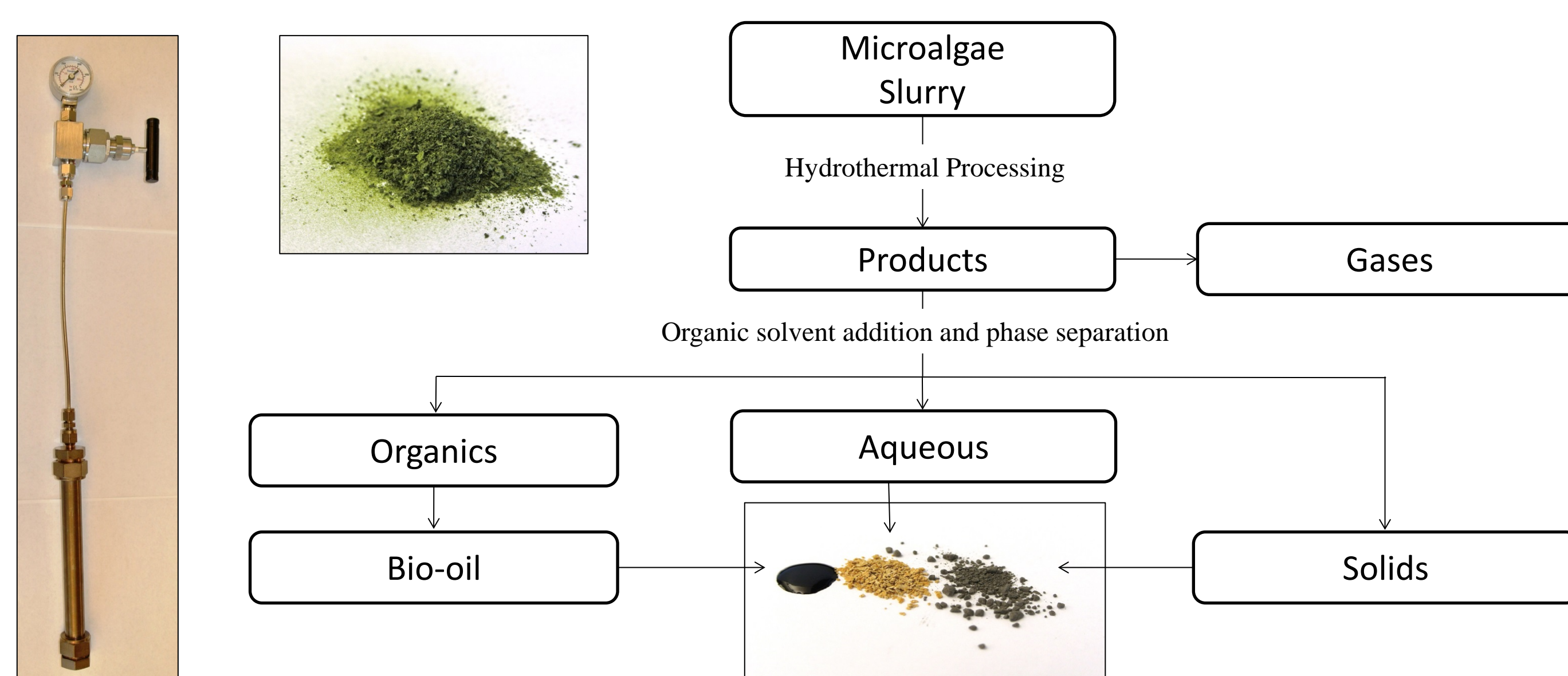
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# Hydrothermal processing of microalgae using inorganic catalysts

## Introduction

- Algae is composed of lipids, proteins, and carbohydrates that can be used for biofuel production with higher photosynthetic efficiency, faster growth rates, and higher area specific yields than terrestrial biomass.
- Hydrothermal processing (HTP) is the decomposition of biomass in the presence of water at elevated temperature and pressure.
- HTP avoids the energy intensive drying process necessary in pyrolysis to convert biomass with high moisture content (80-90%) to fuels.
- Hot compressed subcritical water has fewer and weaker hydrogen bonds, promoting a high availability of H<sup>+</sup> and OH<sup>-</sup> for acid and base catalyzed reactions such as hydrolysis [1].
- Sodium carbonate is a catalyst commonly used in HTP of microalgae to increase the yield and decrease N yields of the bio-oil. Sodium formate and sodium hydroxide are suggested as intermediate compounds resulting from the participation of sodium carbonate with the water-gas shift [2]. The present study compared the catalytic effects of the three related sodium salts during HPT of microalgae with high ash content.

## Materials and Methods



### Microalgae HTP in Batch Reactor:

- Sample: *Chlorella Vulgaris* (3.5 g)
- Solvent: Water (20 mL)
- Catalysts: Sodium carbonate, sodium formate, sodium hydroxide (1.5 g)

### Equipment:

- Stainless steel batch reactors (volume of 32 mL)
- Heating mechanism: Techno Industrial Fluidized Bed 51

### Initial Algae Composition

	Moisture (%)	Volatiles (%)	Fixed C (%)	Ash (%)
Averages	8.9%	61.4%	4.4%	25.3%
St. Dev.	0.6%	3.6%	1.2%	3.4%

### Conditions:

- Reaction temperature: 350°C
- Reaction time: 60 minutes
- Maximum reaction pressure: 24.8 MPa

### Product Recovery Process:

- Product was extracted with 16 mL of dichloromethane
- Solution was then centrifuged to separate water soluble, organic, and solid fractions
- Extraction solvent is evaporated from the organic phase at 50°C for 12 hours
- Aqueous phase was dried at 70°C and solids at 105°C for 24 hours

## Results and Discussion

### Product Yields

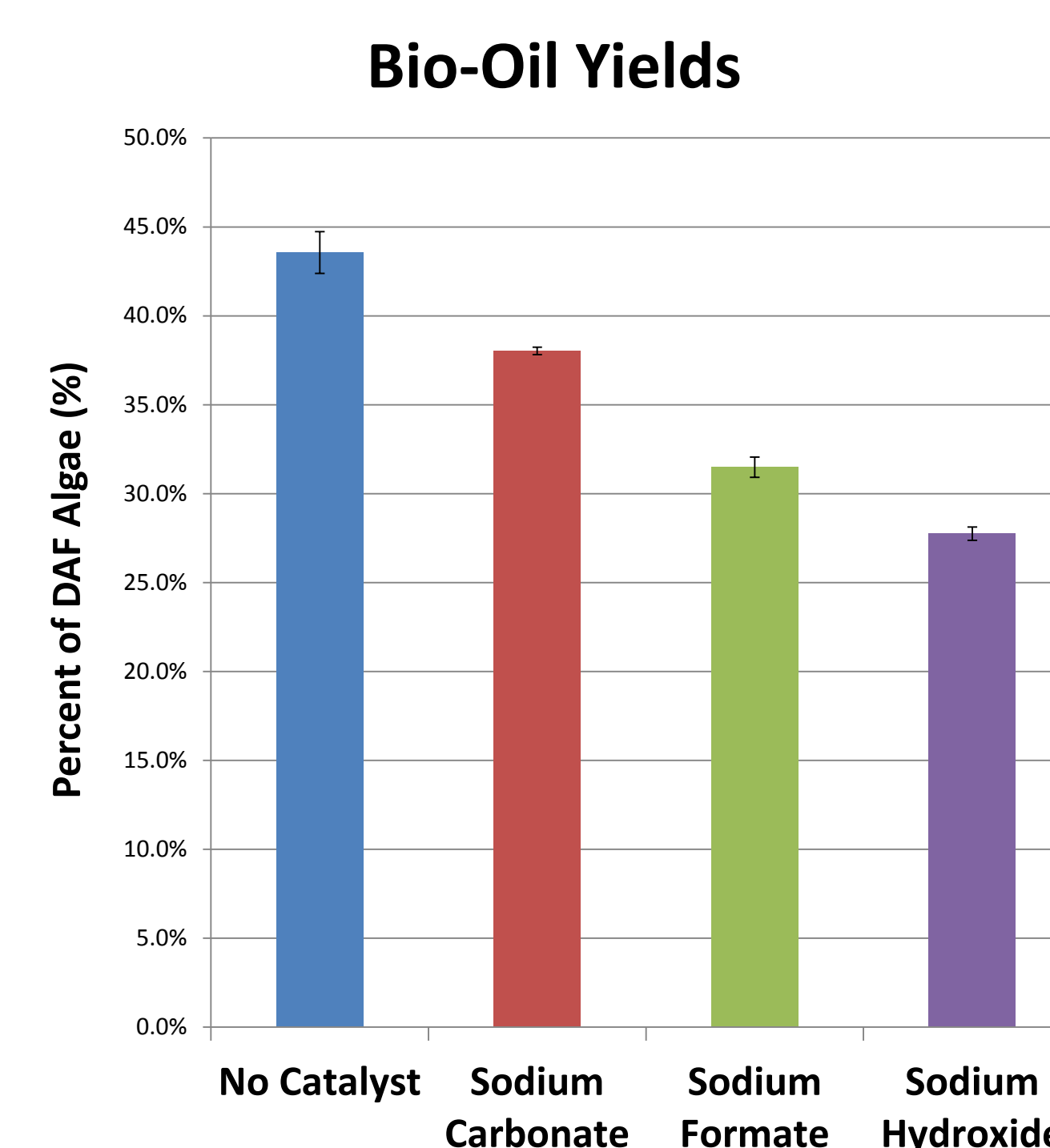
Catalyst	Oil	St. Dev.	Aqueous	St. Dev.	Solids	St. Dev.
No Catalyst	43.6%	1.2%	8.7%*	0.0%	0.4%*	0.3%
Sodium Carbonate	38.0%	0.2%	53.1%*	0.7%	7.3%*	0.8%
Sodium Formate	31.5%	0.6%	46.2%	4.3%	3.2%	0.6%
Sodium Hydroxide	27.7%	0.4%	54.0%	1.0%	8.4%	2.7%

### Bio-Oil Composition

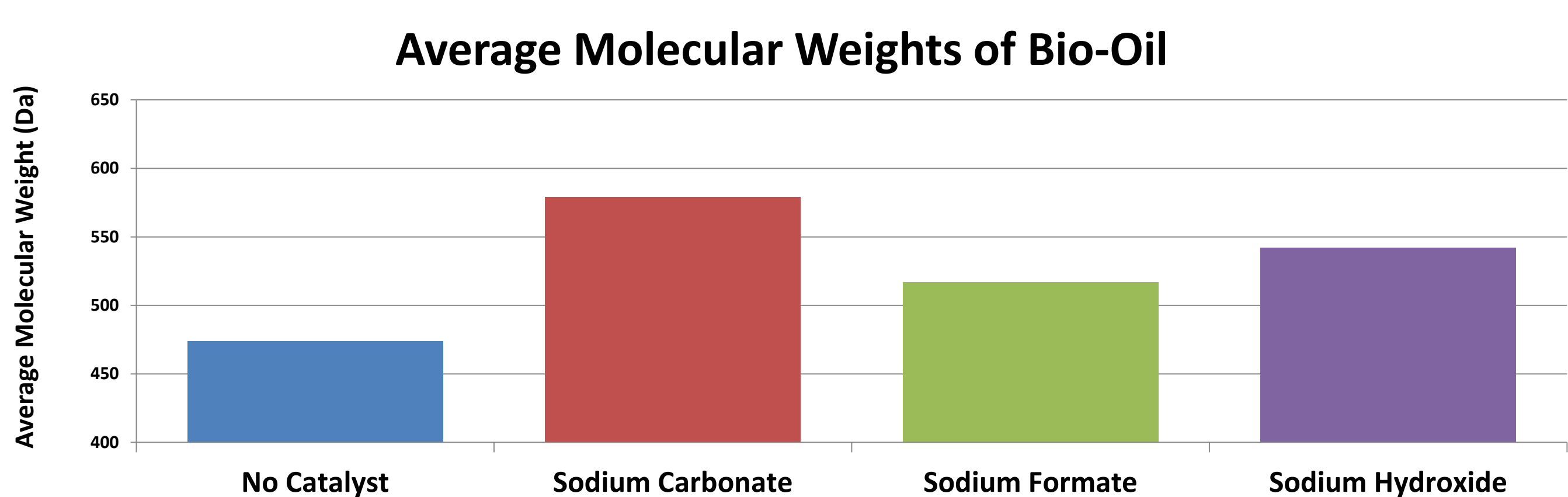
Catalyst	N(%)	C(%)	H(%)	S(%)	O (% by difference)	HHV(MJ/Kg)
No Catalyst	5.92	75.76	7.47	0.45	10.39	34.47
Sodium Carbonate	4.10	78.08	8.14	0.31	9.38	36.36
Sodium Formate	4.84	76.53	8.40	0.26	9.98	36.10
Sodium Hydroxide	3.77	79.06	8.39	0.25	8.54	37.20

Data is on a dry, ash free wt.%  
\*Requires re-run

- The yield of bio-oil reached maximum of 44 wt.% with no catalyst.
- Bio-oil yields from catalytic HTP were overall lower than that from non-catalytic HTP.
- While catalysts are assumed to remain in the solids after the reaction, high yields of the aqueous fraction suggest that catalysts are possibly distributed between solid and aqueous phases after reaction.
- All three catalysts deoxygenated the bio-oil, resulting in bio-oil with higher heating values than the oil produced with no catalyst.
- Sodium hydroxide resulted in bio-oil with the lowest N and highest heating value.



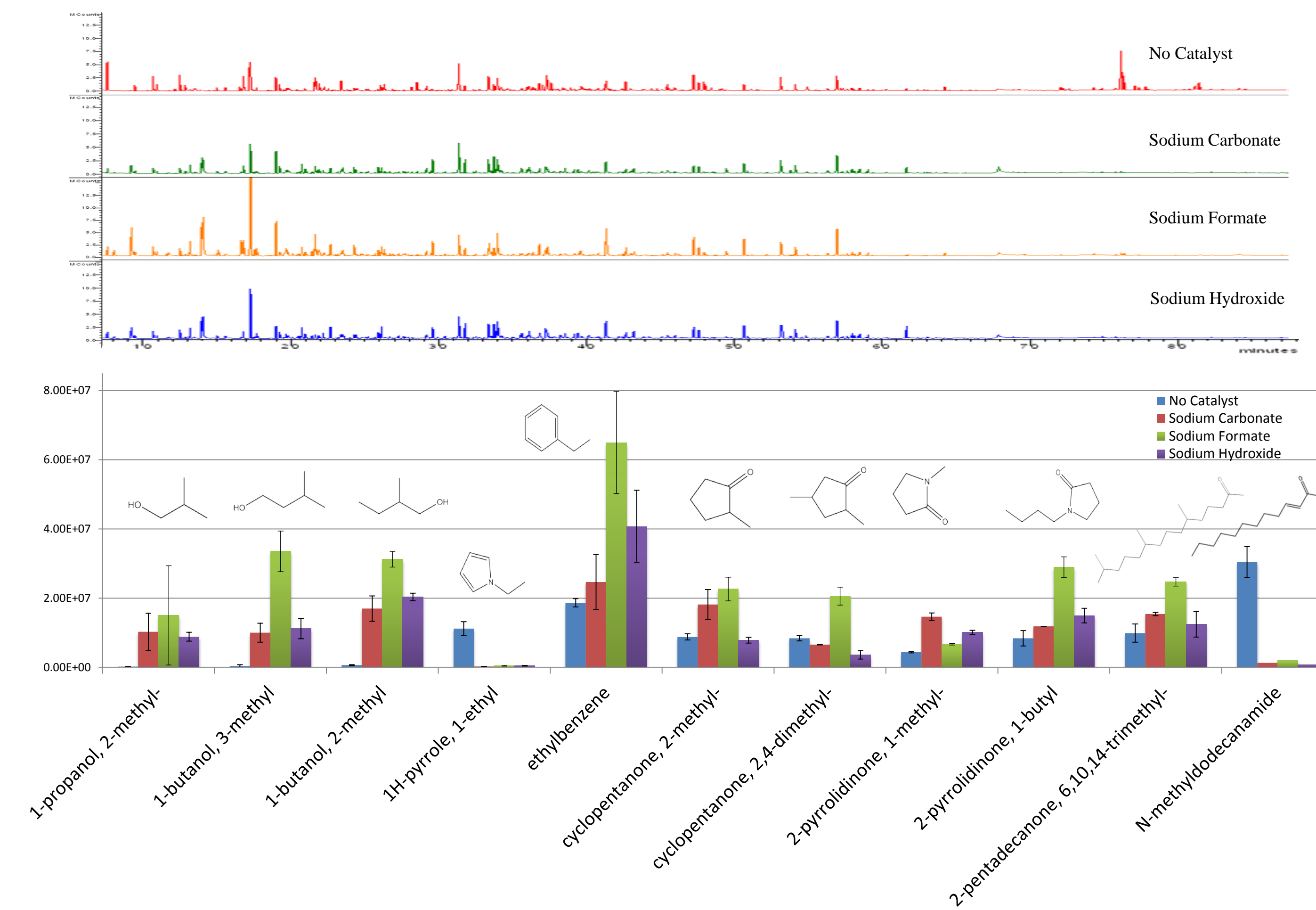
### Average Bio-Oil Molecular Weight



- The average molecular weight ranged from 474 Da to 579 Da
- The bio-oils produced from catalytic HTP have increased molecular weights compared to the bio-oil obtained from non-catalytic HTP. This is possibly because light oxygenates have been removed during the evaporation of the solvent from the bio-oil fraction.

## Results and Discussion

### GC/MS Chromatograms and Compound Yields



- It was found that bio-oil dissolved in dichloromethane provided higher definition of product compounds than when dissolved in acetone (not shown) for GC/MS analysis.
- All three catalysts reduced the nitrogen containing compounds in the oil.
- Sodium formate produced the highest yields of light oxygenates and cyclic pentanones.
- All three catalysts produced a higher yield of light oxygenates, suggesting lower bio-oil yields from catalytic HTP is possibly due to the loss of light compounds during the solvent evaporation process.

## Conclusions

- While all the tested catalysts produced better quality of bio-oil compared to the case with no-catalyst, there were significant differences among the products from each catalyst.
- Sodium carbonate and sodium hydroxide had the strongest effect in removing nitrogen and oxygen in the bio-oil among the four scenarios.
- The overall lower bio-oil yield while using sodium carbonate in this study compared to literature may be a result of the high ash content in the algae and its catalytic effect. Lower bio-oil yields could possibly be due to the loss of light compounds during the solvent evaporation process.
- Challenges arise in the separation of the product fractions when working with HTP. There are many variations in equipment, techniques, feedstocks and solvents used that create lots of variance among different studies. Future studies should consider these factors when performing experiments as well as comparing and analyzing data.

## References

- López Barreiro, D., et al. (2013). "Hydrothermal liquefaction (HTL) of microalgae for biofuel production: State of the art review and future prospects." *Biomass and Bioenergy* 53(0): 113-127.00
- Elliott, D. C. and L. J. Sealock (1983). "Aqueous catalyst systems for the water-gas shift reaction. 1. Comparative catalyst studies." *Industrial & Engineering Chemistry Product Research and Development* 22(3): 426-431.

