Co-processing of fishery and forestry residues – Extracting value from residues

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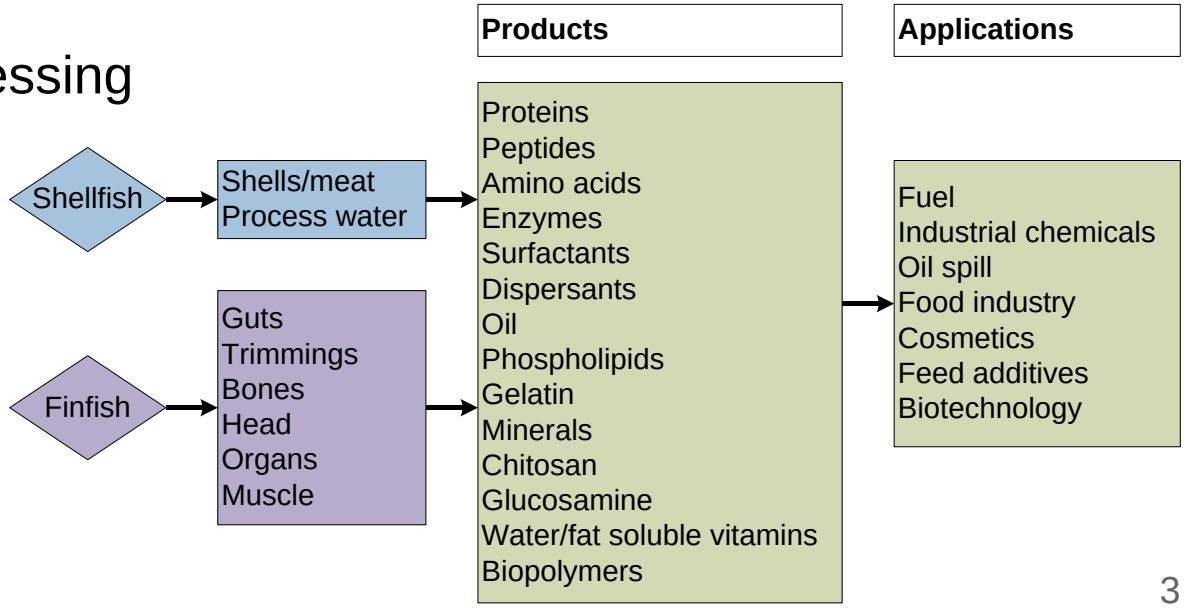
Research focus – Bioproducts from fishery/forestry/agricultural residues

- **Feasibility of any biomass processing to biofuels, biochemicals, or biomaterials driven by**
  - Location and state of feedstock
  - Available infrastructure
  - Distance to market
  - Regional needs
- **Remote/rural operators (forestry, fisheries, mining) face challenges when managing waste/residues**
  - Treatment/storage/disposal costs and transport of residues/wastes high in moisture is costly
  - Limited infrastructure on-site to process/treat waste

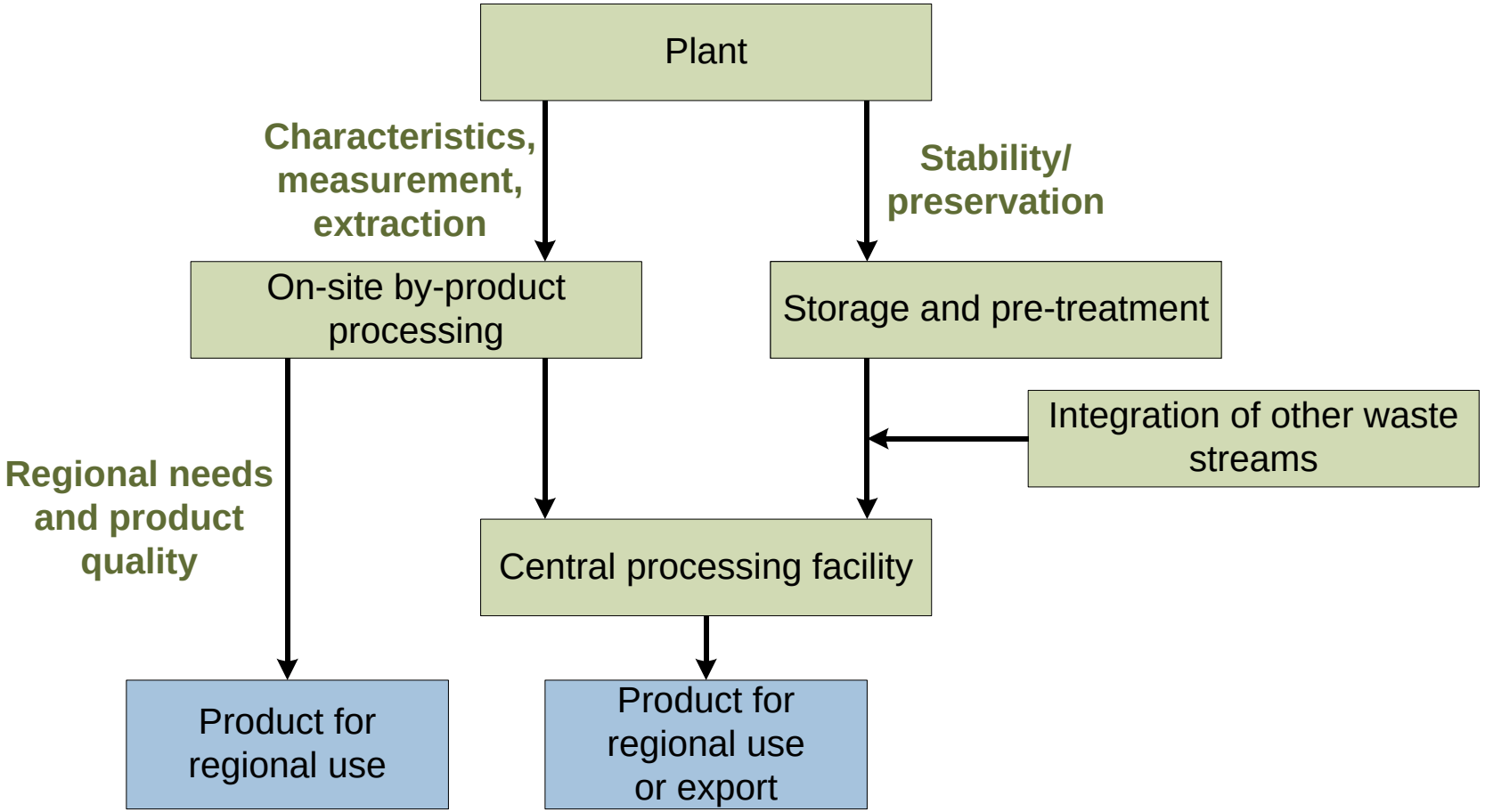
Fish processing waste/by-product

- **By-product volume/composition varies according to:**
  - Species
  - Harvesting
  - Extent of processing
  - Time of year
  - Storage

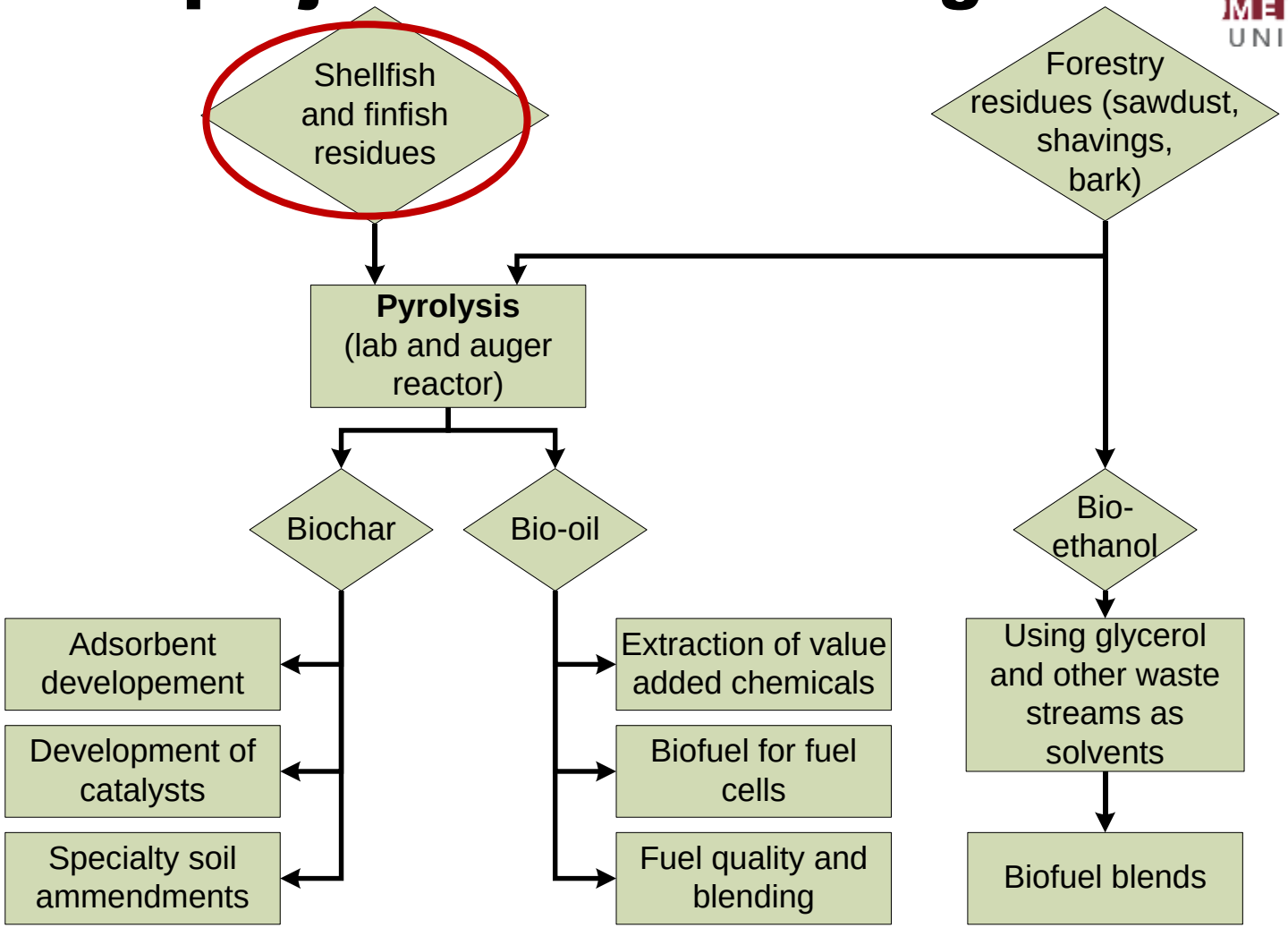
- **E.g. 6 to 8 million tonnes of waste crab, shrimp, and lobster shells produced globally/yr (Mature, 2015)**



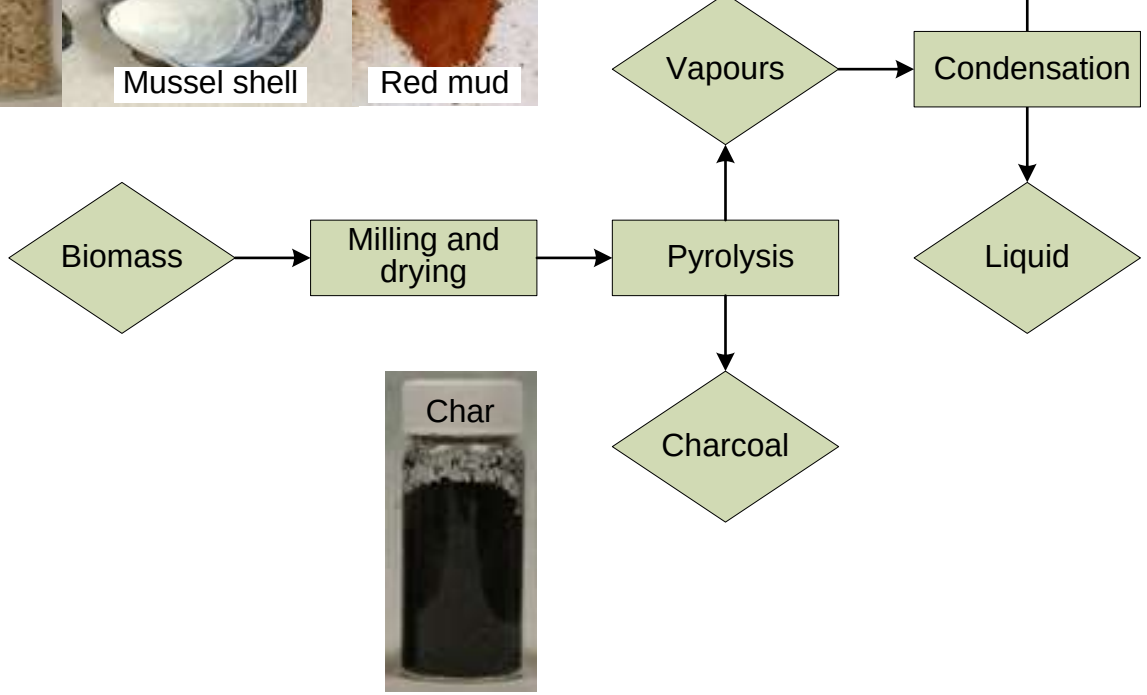
Research approach at MUN
Process Engineering and Chemistry



Current projects in biorefining



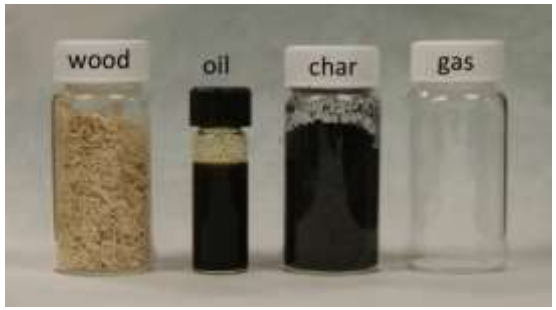
Pyrolysis process



Overview of Process

[1]

[2]



High water & acid content

[3]

Increased energy density

Can we enhance quality of wood derived oil using fishery?

- **Fuel quality of pyrolysis oil**
  - Water levels (20-30%), oxygenated organics, and acidity
  - Degradation with time and high temperature (aging)

- **Process to address quality problems can be expensive and/or complex**

- **Proper design of a process requires better models to predict thermodynamic behaviour (e.g. phase)**

Composition and properties of the oil influenced by

- Feedstock type and ash content
- Pyrolysis temperature
- Biomass particle size
- Reactor type
- Condenser system

Chemical composition

[4-7]

Component	Weight percentage (wt%)
Water	20-30
Aldehydes	10-20
Carboxylic acids	10-15
Carbohydrates	5-10
Phenols (phenol, cresols, guaiacols, syringols)	2-5
Furfurals	1-4
Alcohols	2-5
Ketones	1-5
Lignin degradation products (pyrolytic lignin)	15-30

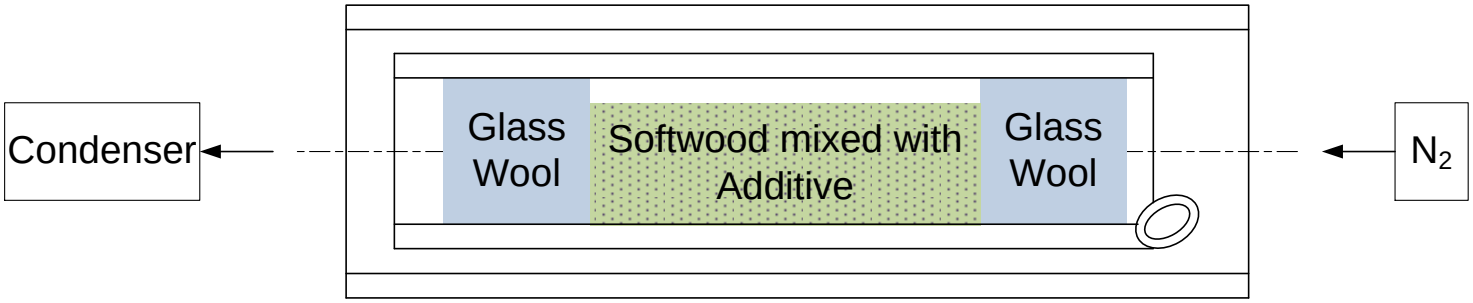
Oil upgrading vs. co-processing

[8]

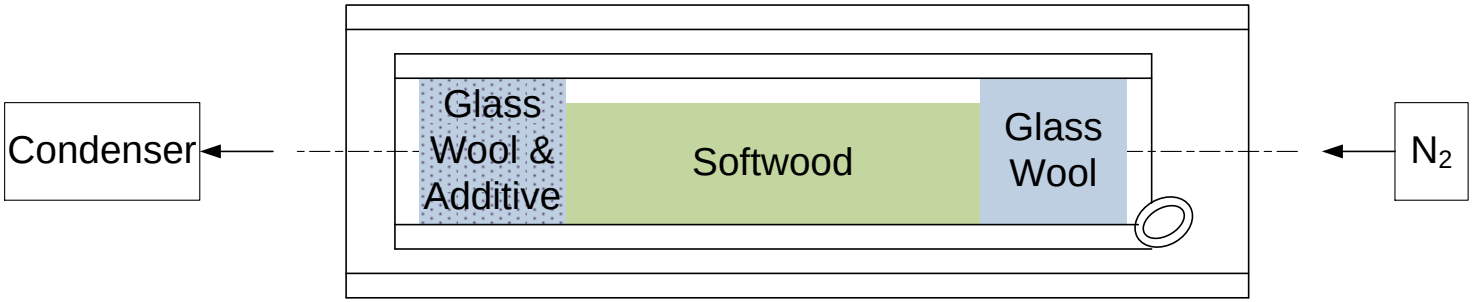
Catalytic upgrading	Co-processing with additive ▪ Additives can be selected to improve oil, char, and gas properties
▪ Catalyst poisoning and deactivation by coke/char and water	▪ Less costly, good performance-to-cost ratio (no catalyst regeneration, atmospheric pressure)
▪ Selective production of certain chemicals (hydrocarbons), higher fuel quality possible	▪ One time use of additive, regeneration difficult/unwanted
▪ High pressure (or vacuum) and hydrogen required	▪ Atmospheric pressure

Tube furnace operational modes

a) *In-situ* or co-pyrolysis



b) *Ex-situ* or vapour upgrading

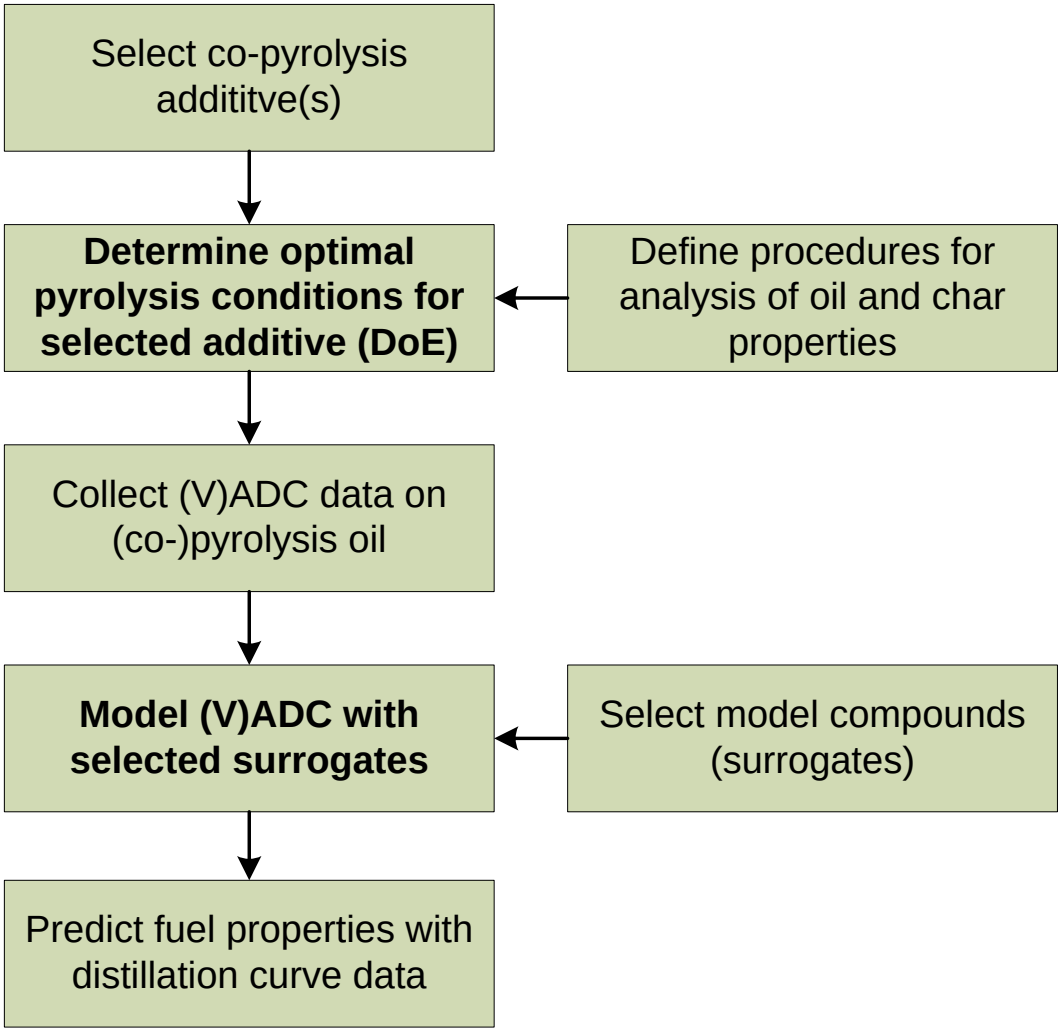


Upgrading during pyrolysis

[10]

Upgrading method	Pros	Cons
Co-pyrolysis	▪ Immediate contact ▪ Intervention in early stage of pyrolysis ▪ Simplified process ▪ Better chance to integrate the reaction heat	▪ Short residence time (1-2 sec) ⇨ Only most active components react ⇨ Limited deoxygenation degree ⇨ Useful for subsequent upgrading ▪ ↑ Additive-to-biomass ratio necessary
Vapour upgrading	▪ Different conditions (p, T, t) for pyrolysis and upgrading ▪ Char separation easier ⇨ Valued solid product ▪ Less additive needed	▪ More reactors ▪ Longer process ▪ ↑ Cost ▪ Process integration inferior

Approach


Select co-pyrolysis adititve(s)
Determine optimal pyrolysis conditions for selected additive (DoE)
Define procedures for analysis of oil and char properties
Collect (V)ADC data on (co-)pyrolysis oil
Model (V)ADC with selected surrogates
Select model compounds (surrogates)
Predict fuel properties with distillation curve data

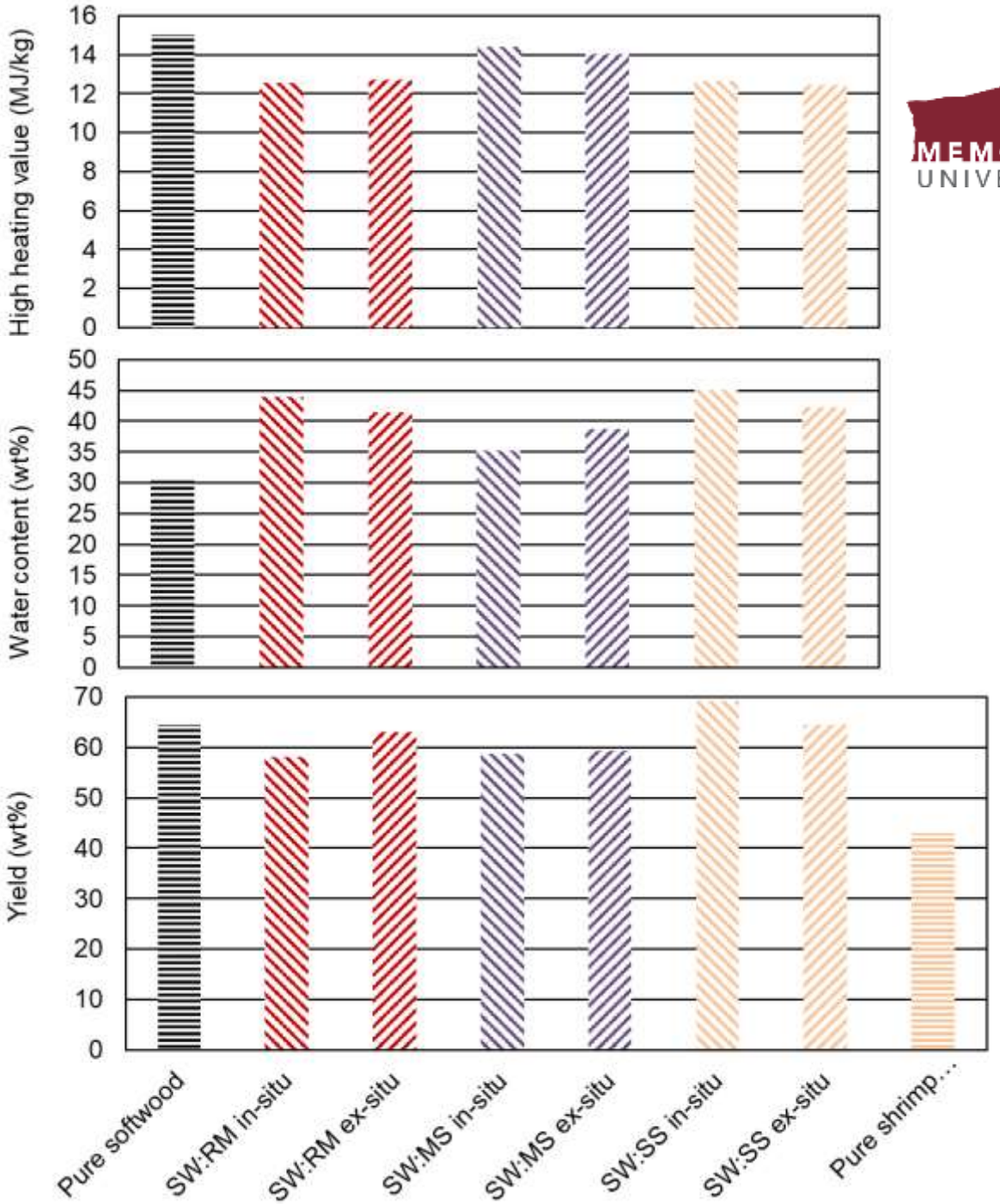
Objectives – Co-pyrolysis

- **Co-pyrolysis of softwood with waste/residues from fisheries or mining**
- **Compare fuel properties**
  - Heating value
  - Water content
  - pH or total acid number (TAN)
  - Viscosity
  - Density
  - Heat capacity
  - Possibly flash/pour point, and solid/ash content

Co-pyrolysis with other residue streams

- **Less costly and more sustainable option compared to catalyst additives and catalytic oil upgrading**
- **Selected additives that could improve oil and/or char properties**
  - Red mud (RM)
  - Mussel shells (MS)
  - Shrimp shells (SS)
- **Two sets of preliminary experiments**
  1. Py-GCMS
  2. Tube furnace experiments

Results Additive Tests



Experiments

- **Based on screening studies**
- **Co-pyrolysis of softwood with mussel shell**
- **Varied 4 parameters**
  - Temperature (400-525 °C)
  - Nitrogen flow (50-300 ml/min)
  - Operational mode (*ex-situ*, *in-situ*)
  - Softwood-to-additive ratio (0-50 wt% mussel)

- **Oil and char analysis**

Results DoE

- **Temperature 500 °C**
- **Nitrogen flow 50 mL/min**

	Mussel shell (wt% of feed)	
	0	**50**
Yield oil (wt%)	62	58
Water content (wt%)	28.5	39
HHV (MJ/kg), *in-situ*	16	14.5
HHV (MJ/kg), *ex-situ*	15.3	14
TAN (mgNaOH/gOil), *in-situ*	68	48
TAN (mgNaOH/gOil), *ex-situ*	65	56

Conclusion and future work

- **Preliminary co-pyrolysis work shows waste mussel shell can improve oil quality**
  - Reduce TAN from 68 to 48 mgNaOH/gOil
- **ADC experiments and modeling ongoing**
- **Design of scaled up system**

Acknowledgements

References

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Thank you for your attention.