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Challenges and opportunities for the synthesis of novel pyrolysis oil refineries

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Pyroliq2019

Challenges and Opportunities for the Synthesis of Novel Pyrolysis Oil Refineries

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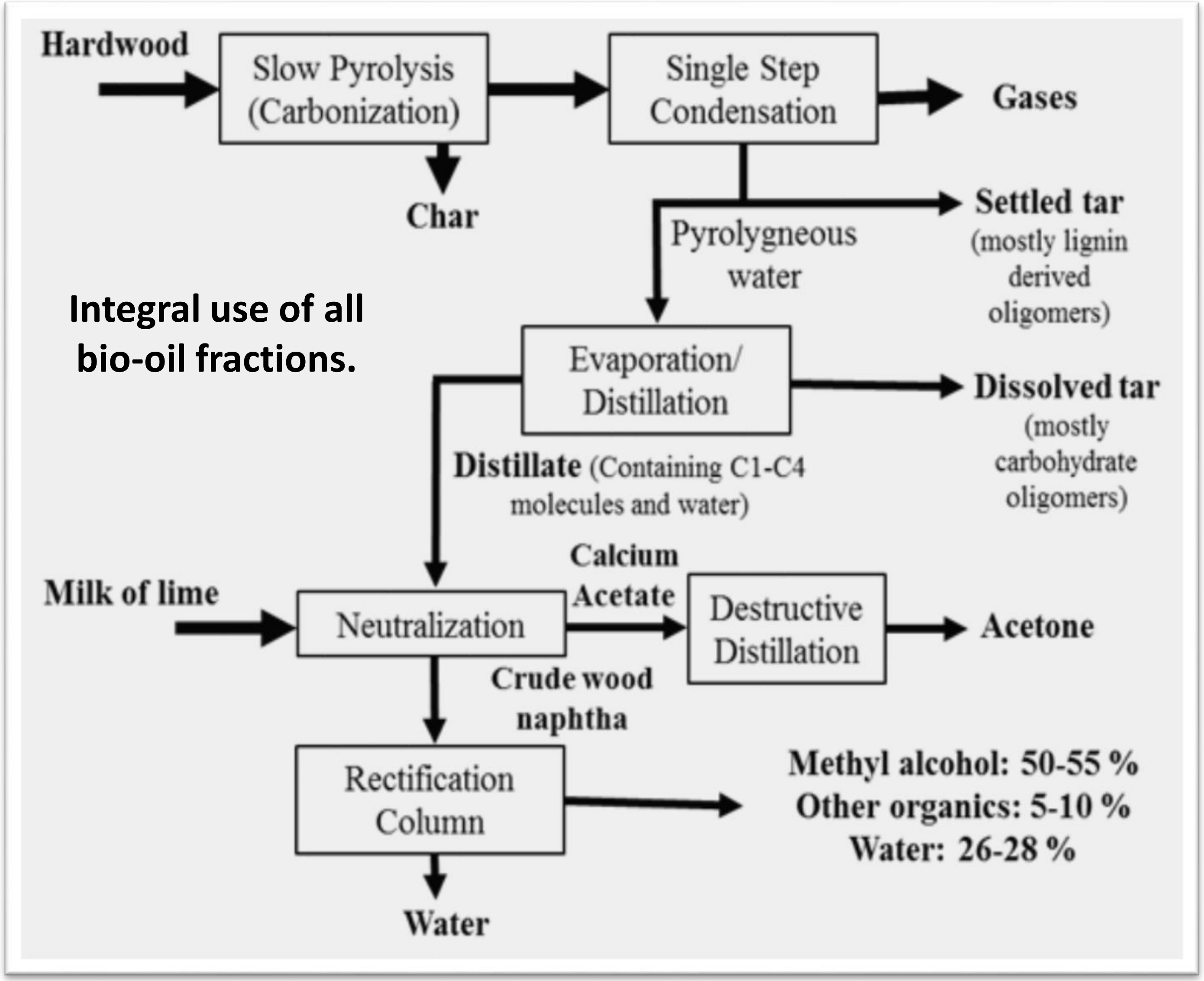
Motivation: Bio-oil Refinery Concepts

Wood Distillation Industry:

- 19th and early 20th century
- Production of charcoal, tars, acetone, and wood naphtha (C1-C4)
- Mostly from hardwood.

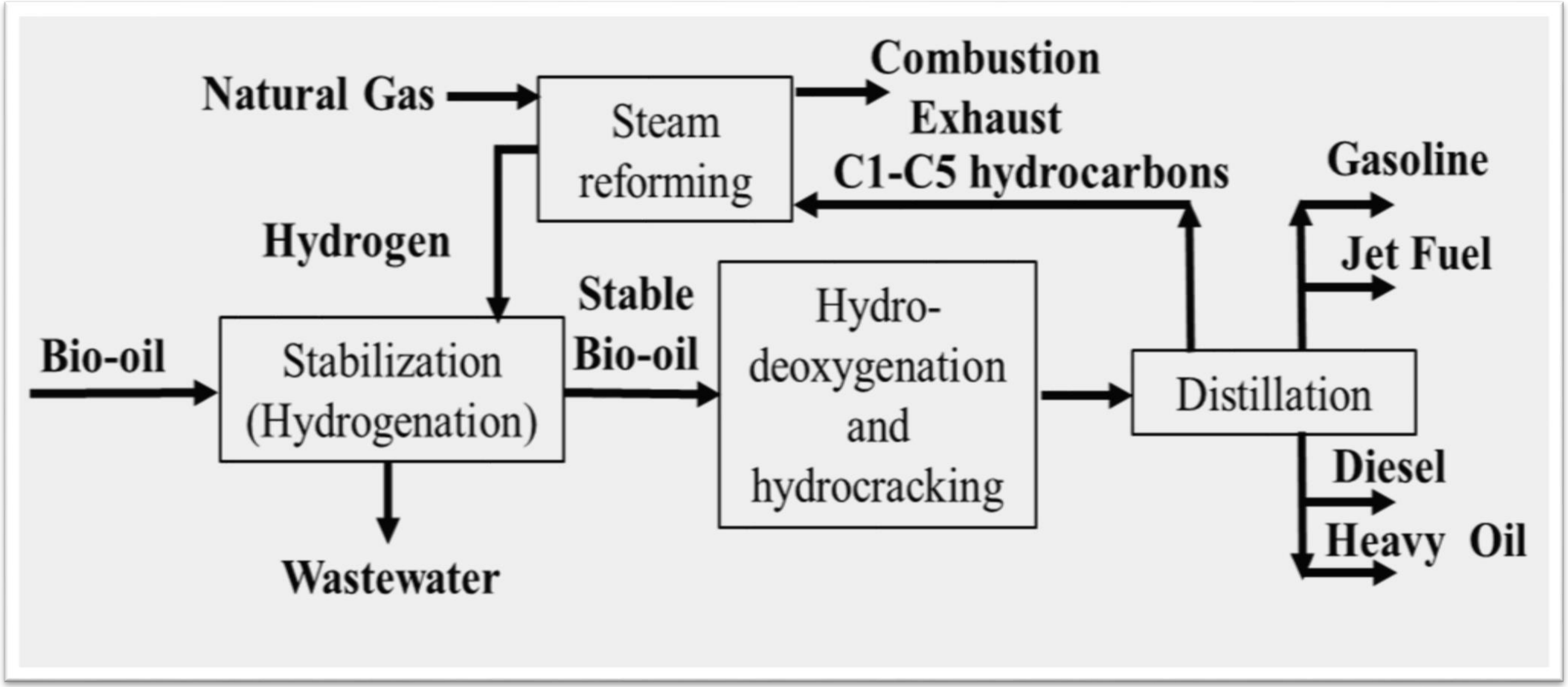


Pinheiro Pires AP, Arauzo J, Fonts J, Domine ME, Fernandez-Arroyo A, Garcia-Perez ME, Montoya J, Chejne F, Pfromm P, Garcia-Perez M: Challenges and Opportunities for Bio-oil Refining: A review. *Energy Fuels*, **2019** (In press)

Motivation: Bio-oil Refinery Concepts

Two-Step Hydrotreatment

- Pacific Northwest National Lab (PNNL): Bio-oil hydrotreatment using $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$ (petroleum processing catalysts)



Motivation: Bio-oil Refinery Concepts

Two-Step Hydrotreatment

To ensure economic competitiveness, bio-oil price needs to be a fraction of molasses ($ 300-400/ ton) and petroleum ($ 200-700/ton). Bio-oil production cost needs to be below **$ 150/t**.

In our analysis we used the recommendations made by Lange (2016)

Product cost ~ (feed Price + conversion cost) / yield

Feed Price: $ 150/ ton_{feed}

Conversion Cost: $ 200/ton_{feed}

Yield: 0.33 ton fuel/ton_{feed}

Product Cost: $ 1060/ton_{feed}

Gasoline market: $ 700-800/ton_{feed}

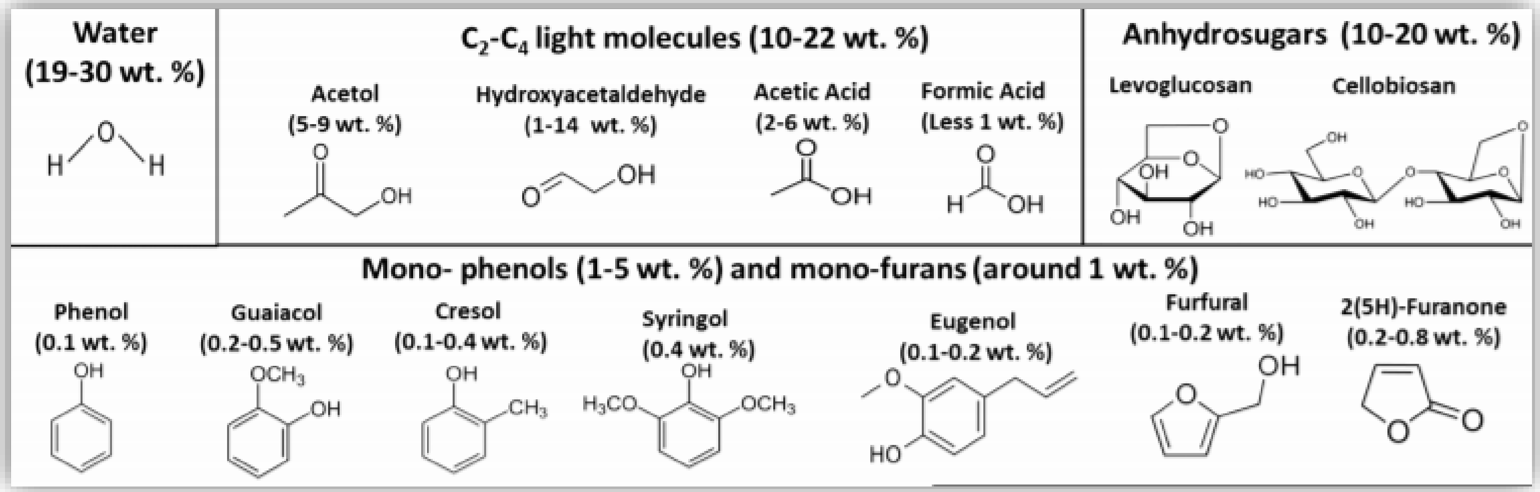
Lange JP. Catalysis for biorefineries – performance criteria for industrial operation. Catal. Sci. Technol. 2016, 6, 4759

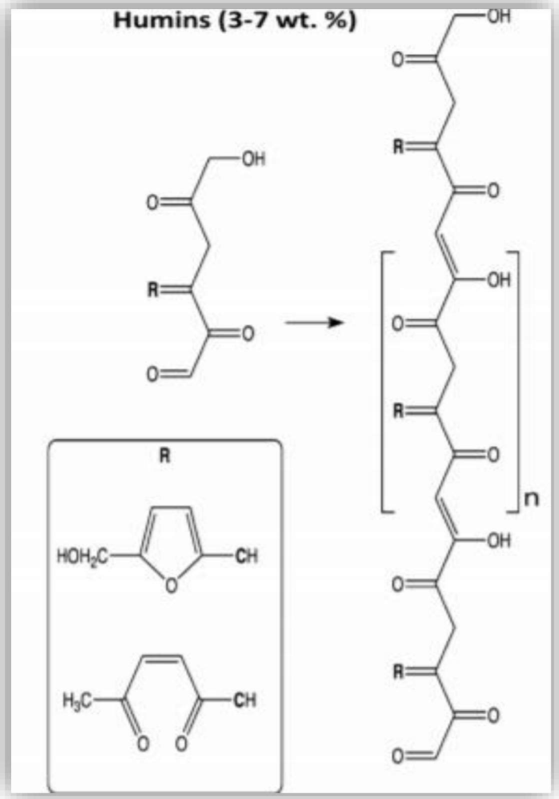
Hurdles

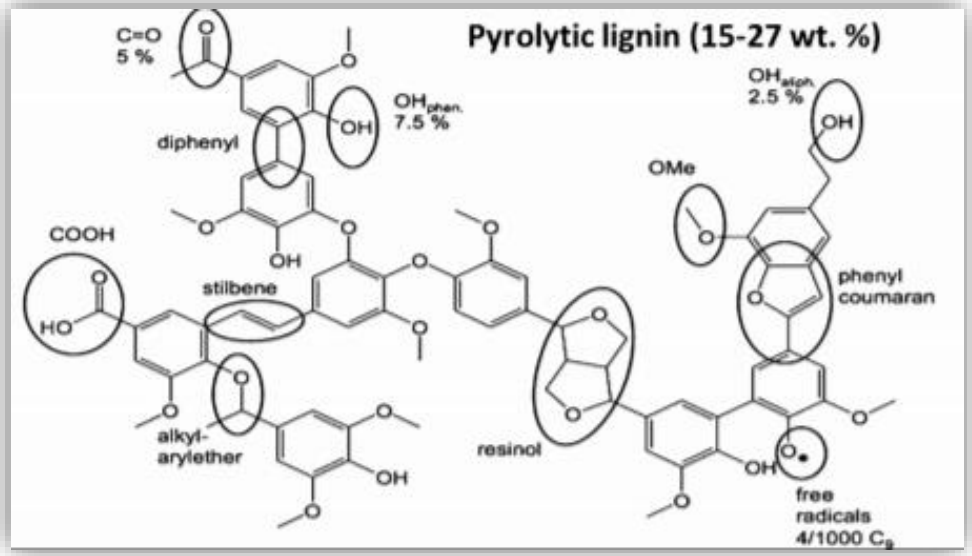
- High oxygen content – reactivity – low thermal stability during storage, handling, and upgrading
- Requires more separation steps than conventional petroleum
- Two step hydrotreatment biorefinery: minimum selling prices too high: more than $ 1000/ton (gasoline: $700-800 t^{-1})
- Bio-oil deoxygenation is fundamentally an emerging, poorly known and very expensive unit operation
- To achieve yields of 33 % the carbon conversion efficiencies have to be higher than 70 %. It will be very difficult to increase yield.
- High hydrogen consumption (close to 6 g H_2/100 g bio-oil)
- Lack of High value product
- Final fuel is rich in aromatics

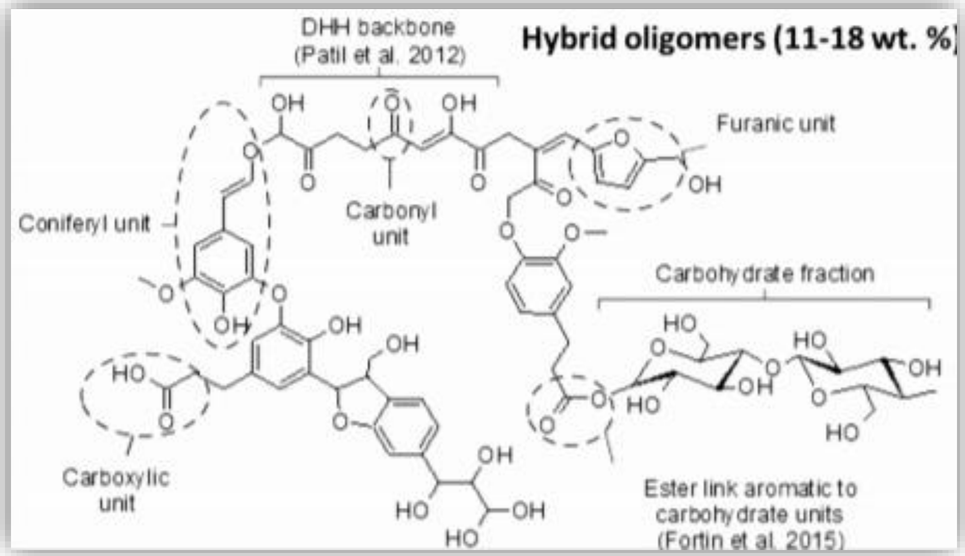
Bio-oil

Representative molecules of bio-oil fractions



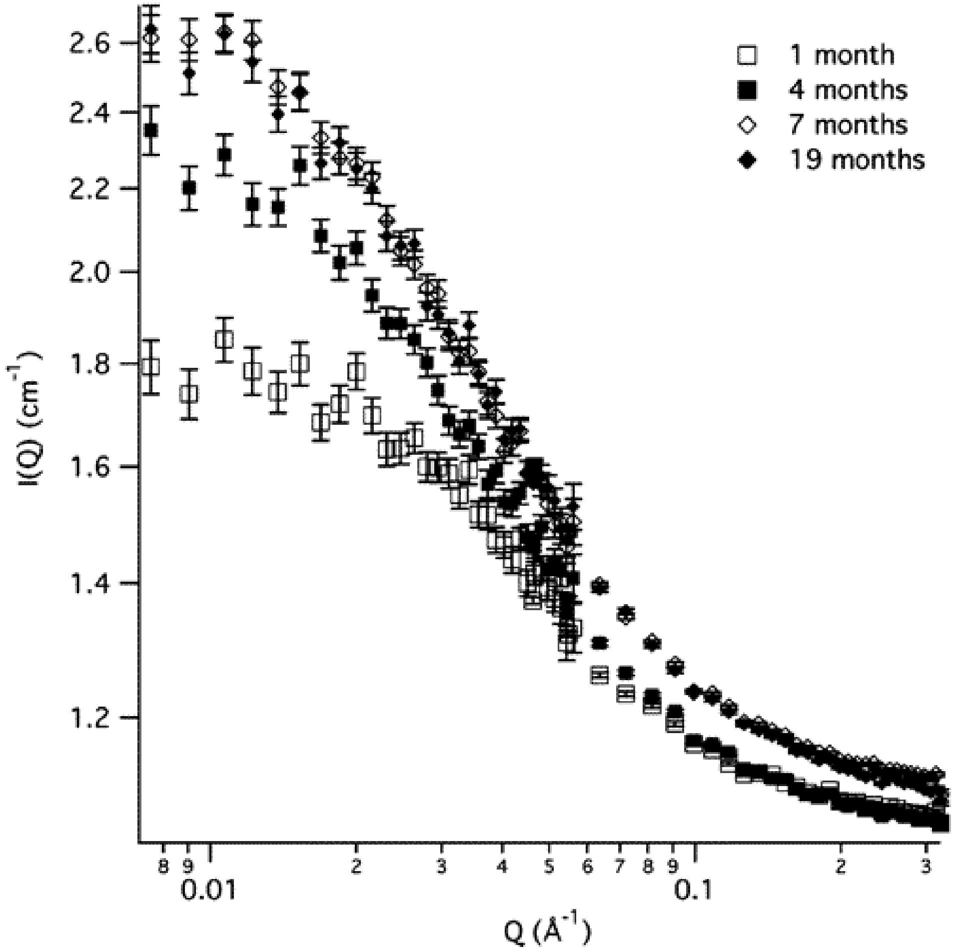




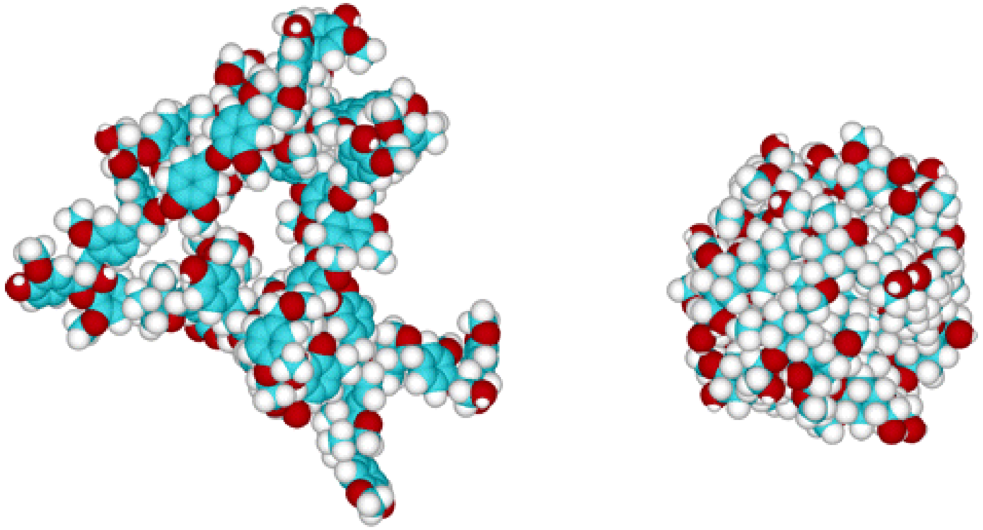


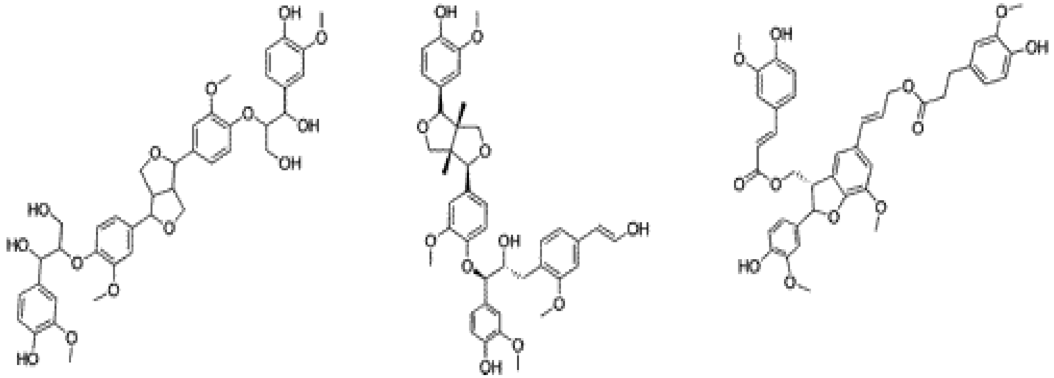
Bio-oil

SANS intensity distribution for 1-, 4-, 7-, and 19 months old sample.



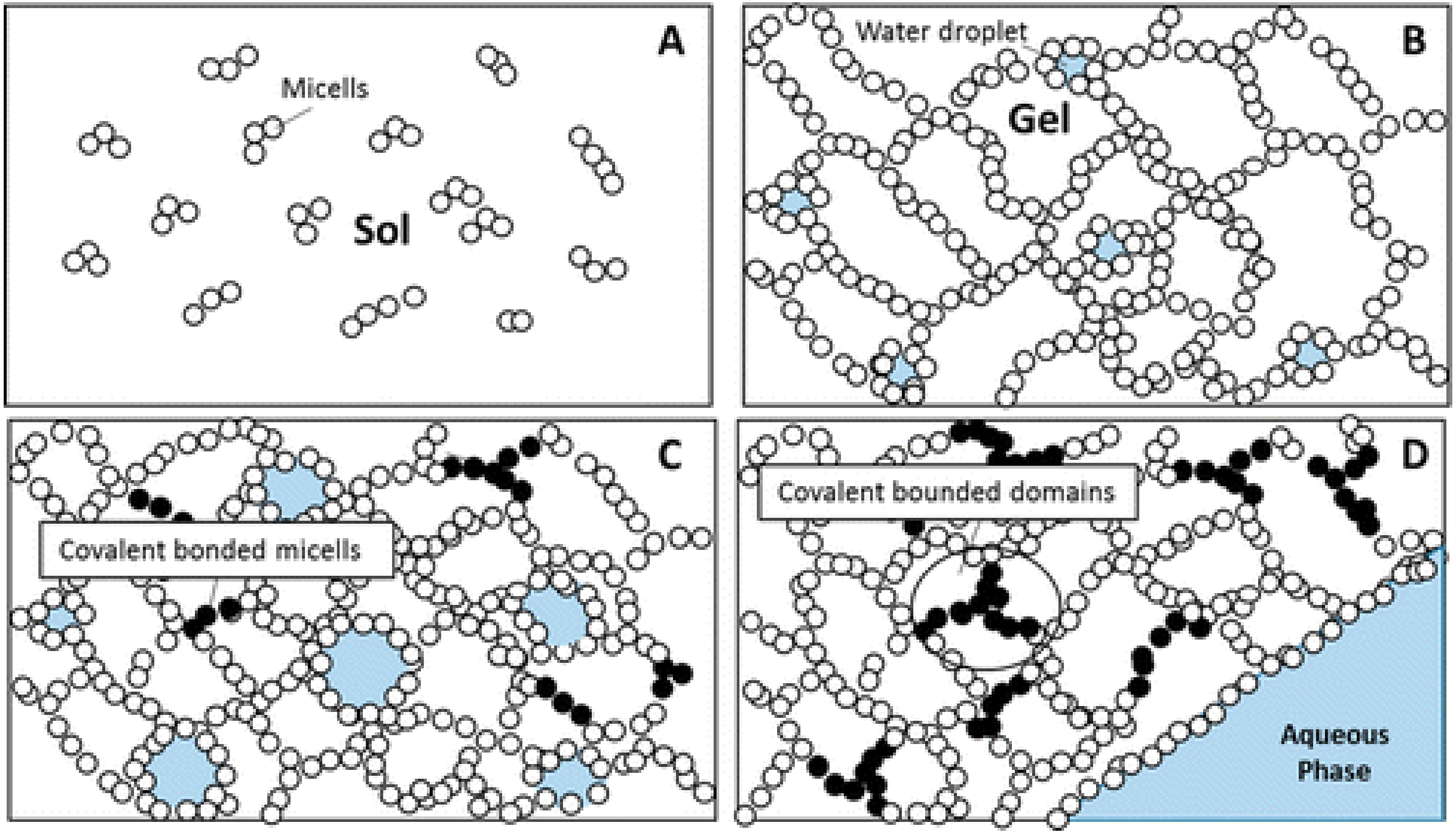
Three dimensional structure of Pyrolytic lignin molecules





Frantini E, Bonini M, Oasmaa A, Solantausta A, Teixeiro J, Baglioni P: SANS Analysis of the Microstructural Evolution during the Aging of Pyrolysis Oil from Biomass. Langmuir, 2006, 22 (1), 306-312.

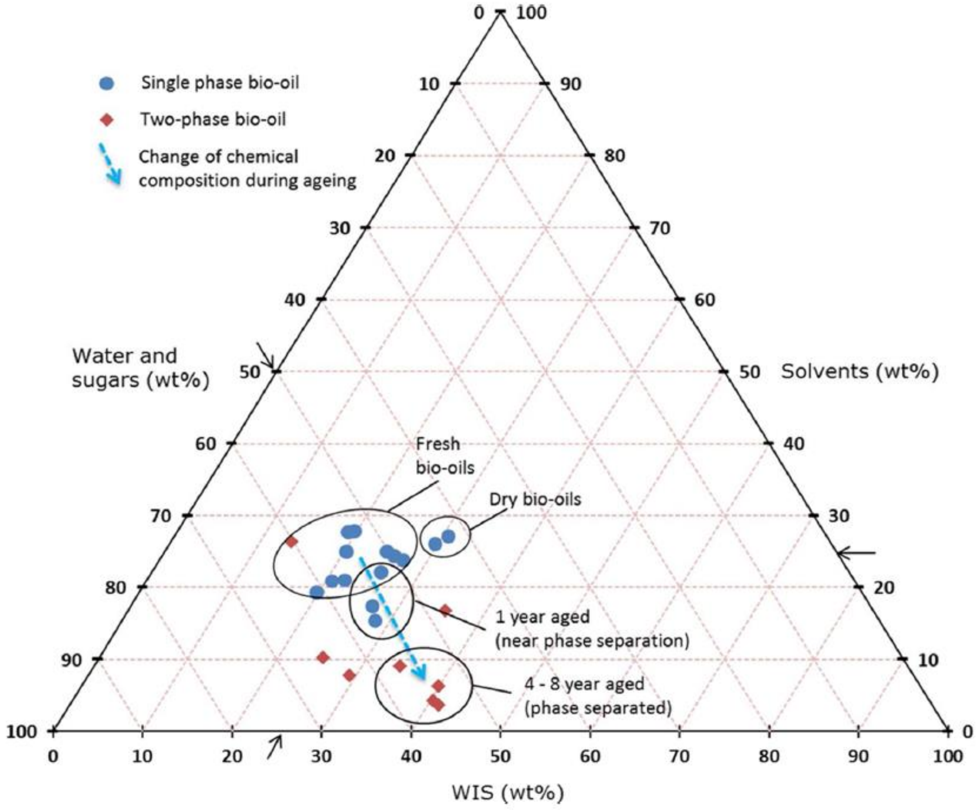
Bio-oil

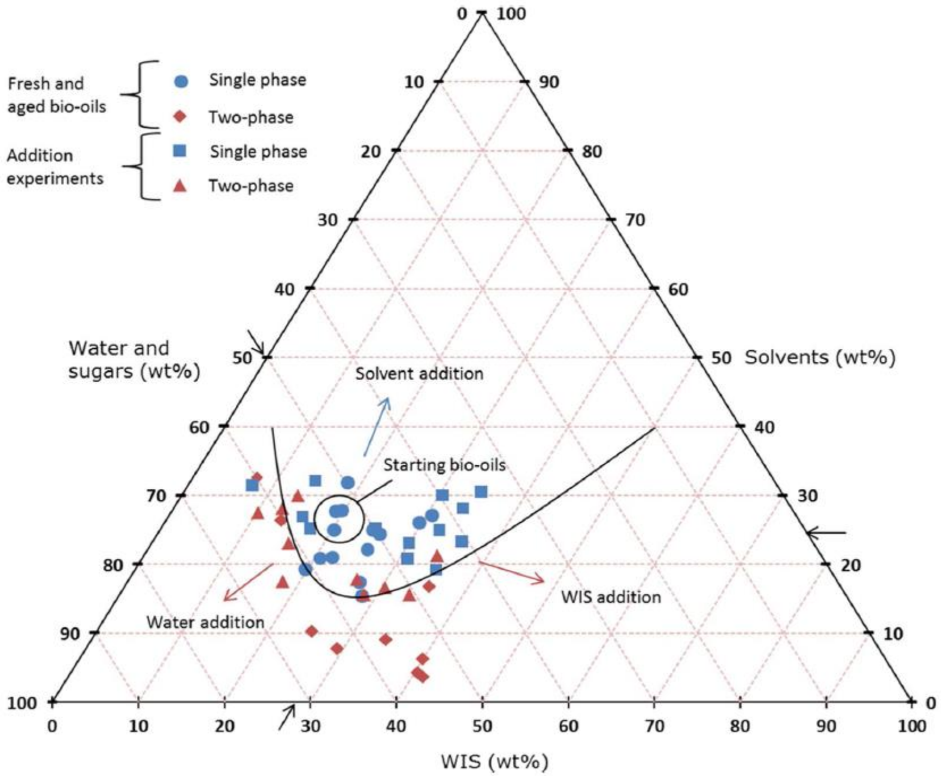


Oasmaa A, Fonts I, Pelaez-Samaniego MR, Garcia-Perez ME, Garcia-Perez M: Pyrolysis Oil Multiphase Behavior and Phase Stability: A Review. Energy Fuels, 2016, 30 (8), 6179-6200

Bio-oil

Liquid – Liquid Equilibrium Diagrams





$$\text{stability index} = \frac{10.66\text{WIS} \times e^{(-0.0611\text{WIS})}}{\text{water} + \text{sugars}}$$

Oasmaa A, Sundqvist T, Kuoppala E, Garcia-Perez M, Solantausta Y, Lindfors C, Paasikallio V: Controlling the Phase Stability of Biomass Fast Pyrolysis Bio-oils. Energy Fuels **2015**, 4373-4381

Bio-oil

Very complex mixture with hundreds of compounds with concentration below 0.5 wt. %

↓

Only **glycolaldehyde, acetic acid, acetol and levoglucosan** (and methanol, if hardwood is used as feedstock) have concentration high enough (>5 wt %) to justify their separation as chemicals

↓

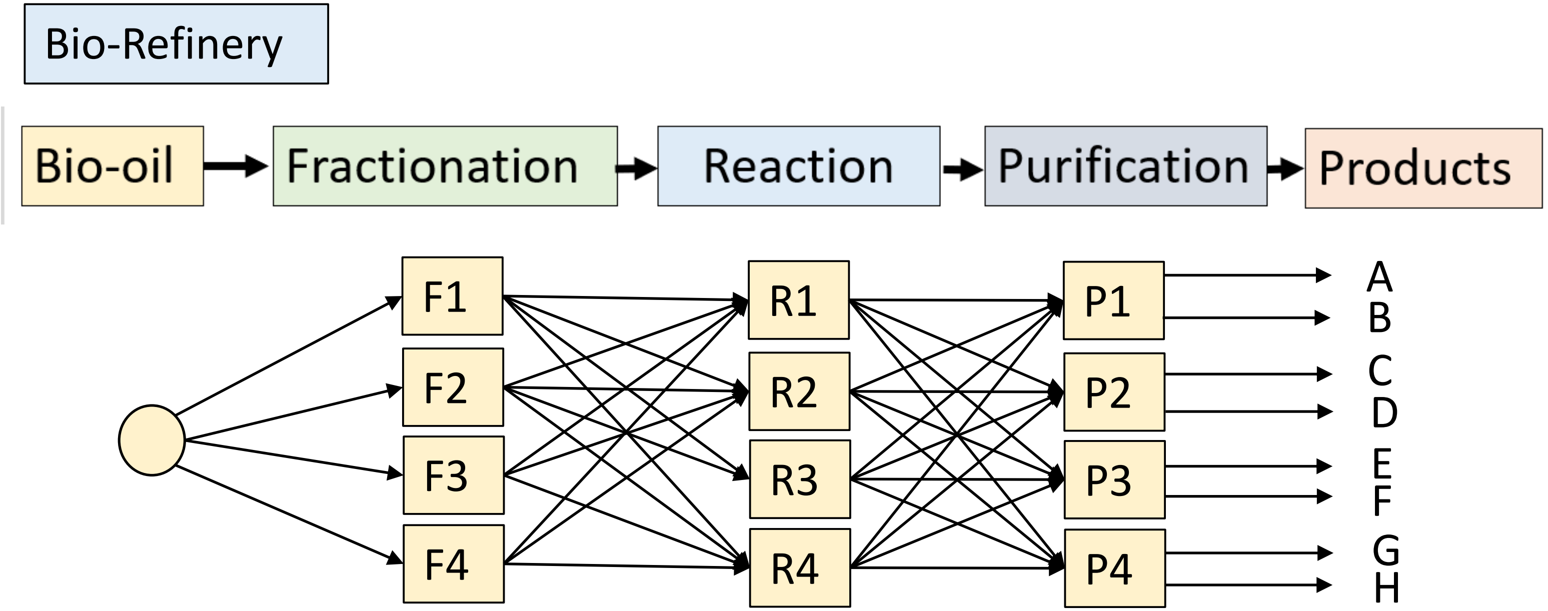
The rest of the compounds have to be commercialized in fractions (**monophenols, sugars, lignin oligomers, pyrolytic humins, hybrid oligomers**)

Bio-oil Refinery Conceptual Frame

Bio-oil → Fractionation → Reaction → Purification → Products

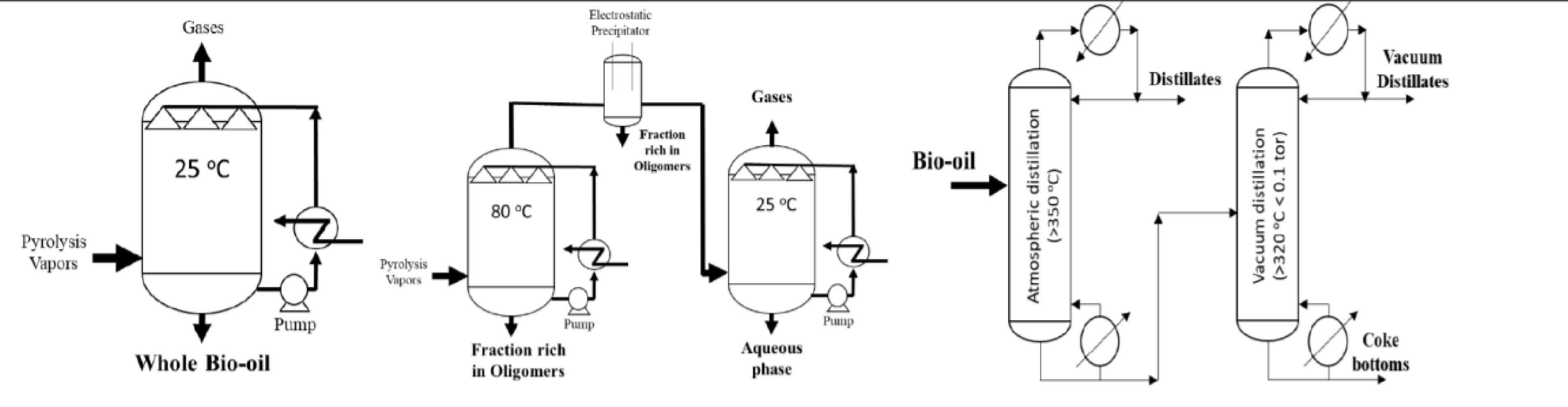
- A Water
- B Methanol
- C Acetol
- D Hydroxyacetaldehyde
- E Acetic Acid
- F Mono-phenols
- G Levoglucosan
- H Heavy anhydrosugars
- I Pyrolytic humins
- J Pyrolytic Lignins
- K Hybrid Oligomers

??? ??? ??? ???

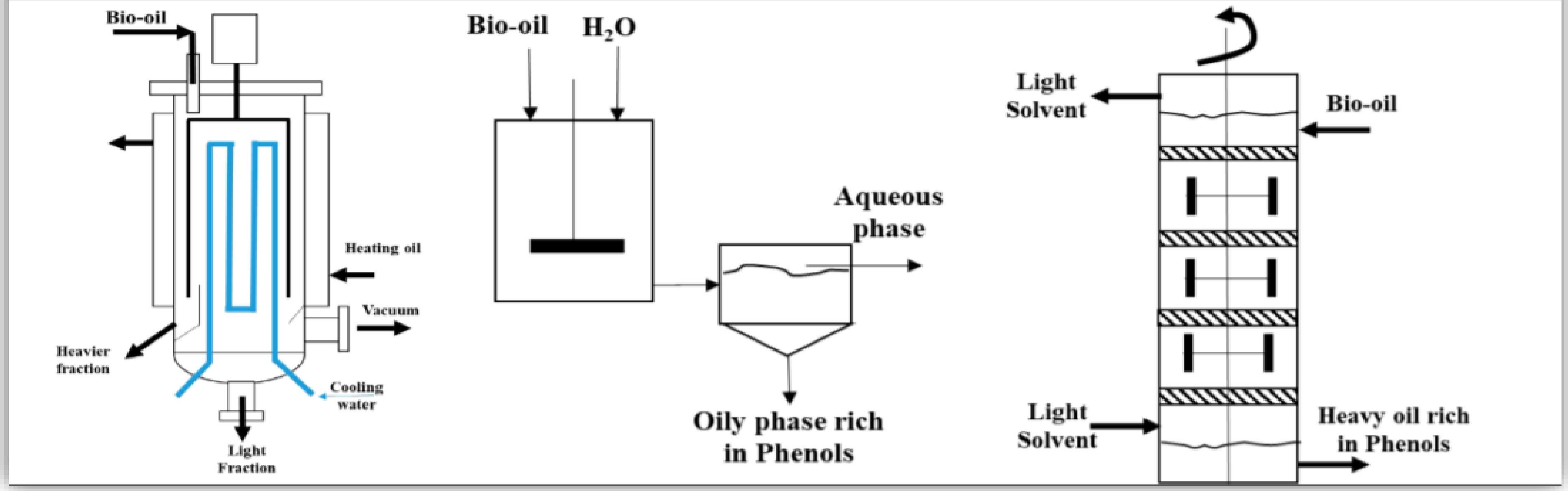


Bio-oil Fractionation Strategies

(a) Single condensation Step, (b) Fractional Condensation and (c) Distillation (atmospheric+ vacuum)

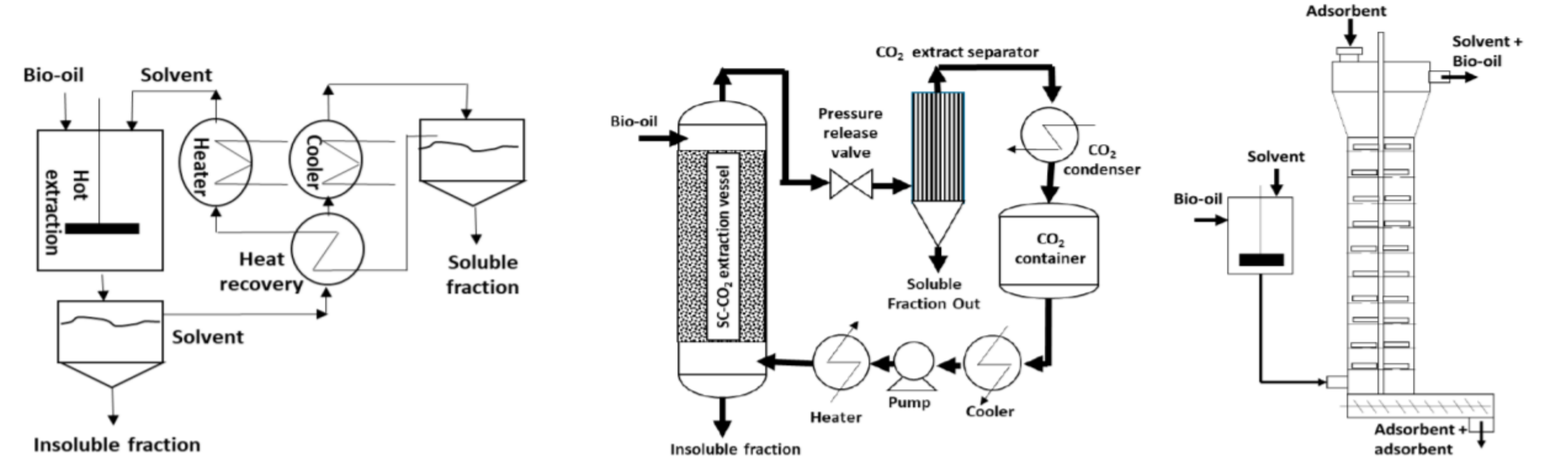


(d) Molecular distillation, (e) Water extraction and (f) Solvent extraction

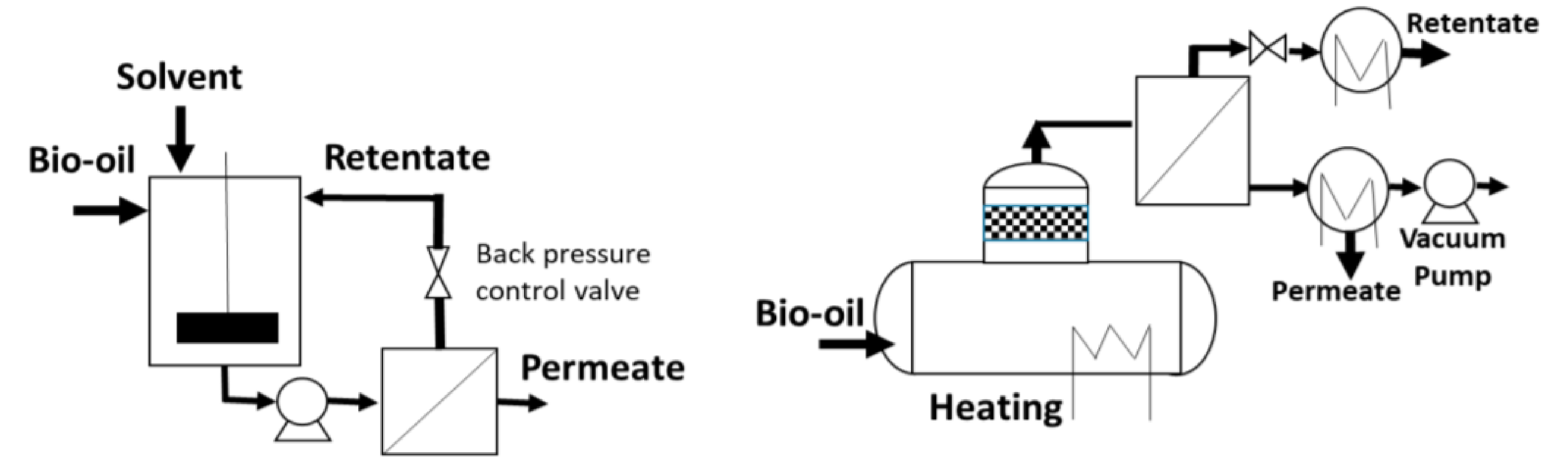


Bio-oil Fractionation Strategies

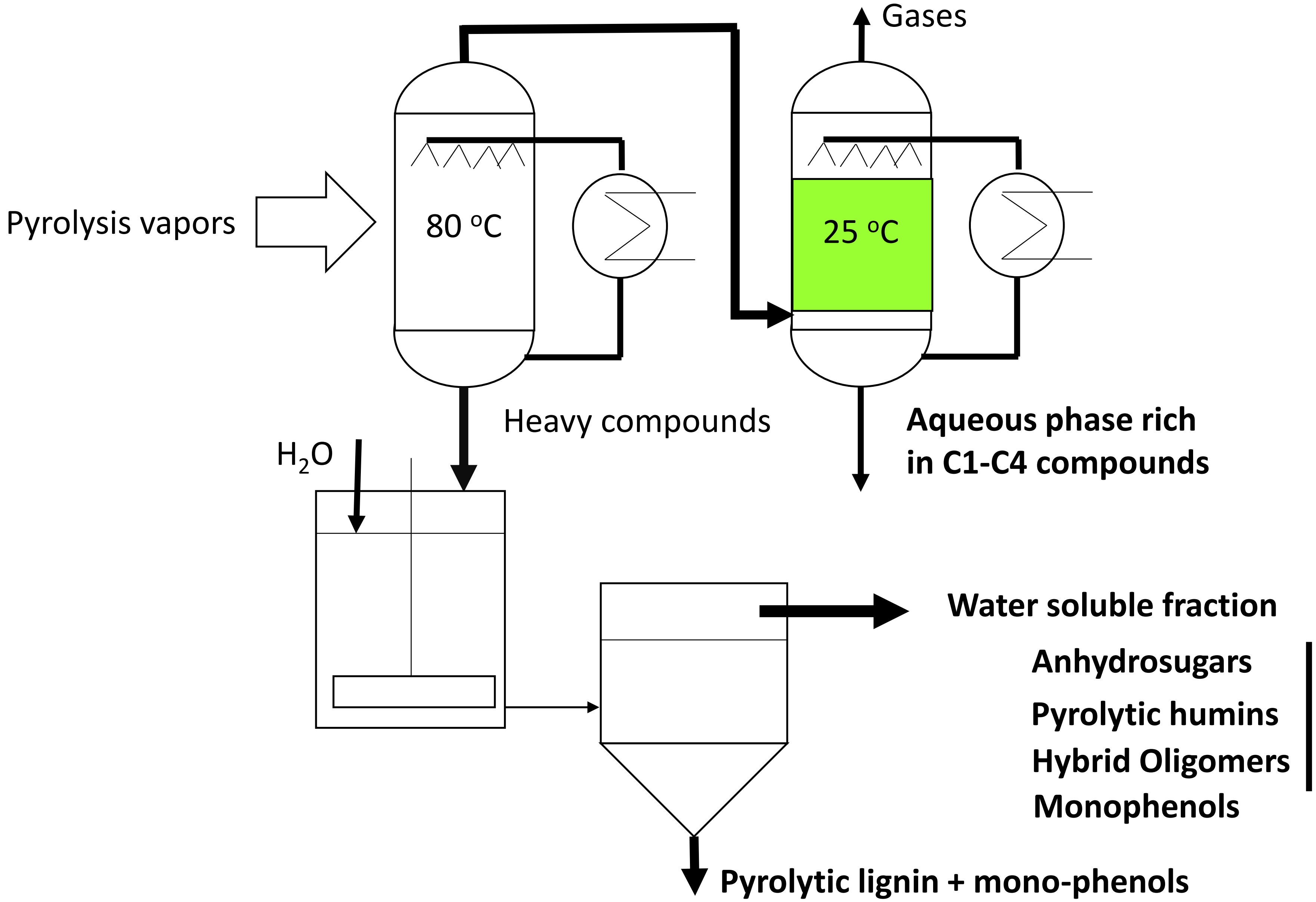
(g) Temperature Swing extraction, (h) supercritical CO_2 extraction, (i) Solid-liquid extraction



(j) Nano-filtration, (k) Pervaporation



Bio-oil Fractionation Strategies



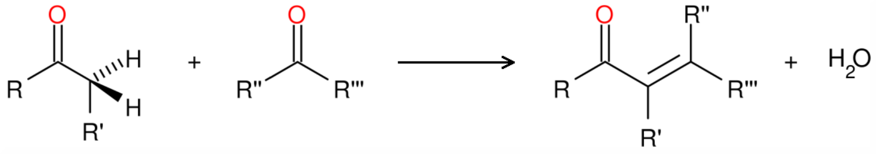
No technique available to fractionate the water soluble fraction

Reactions

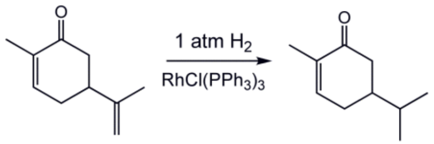
Ketonization[1]

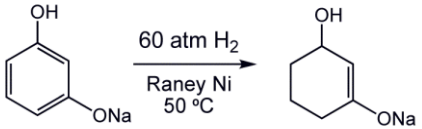
$$R_1COOH + R_2COOH \rightarrow R_1COR_2 + CO_2 + H_2O$$

Aldol Condensation

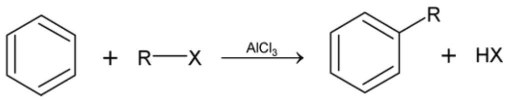


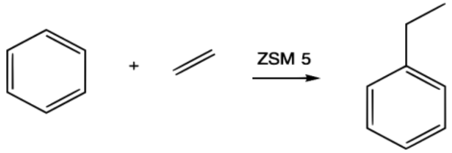
Hydrogenation





Alkylation

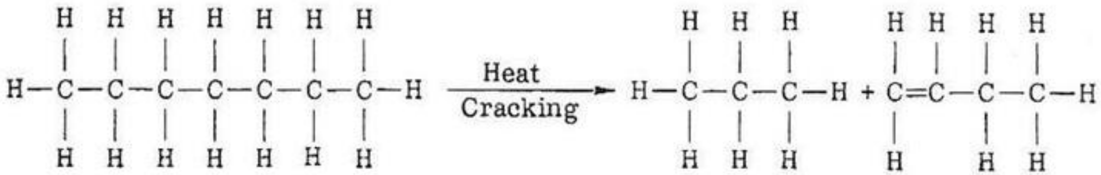


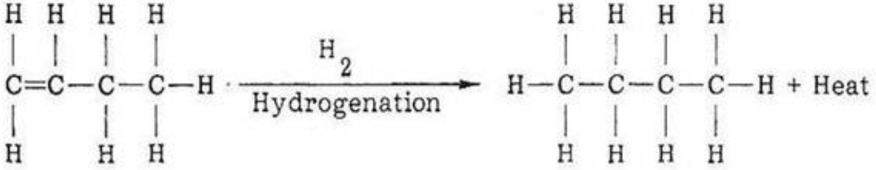


Hydro-deoxygenation

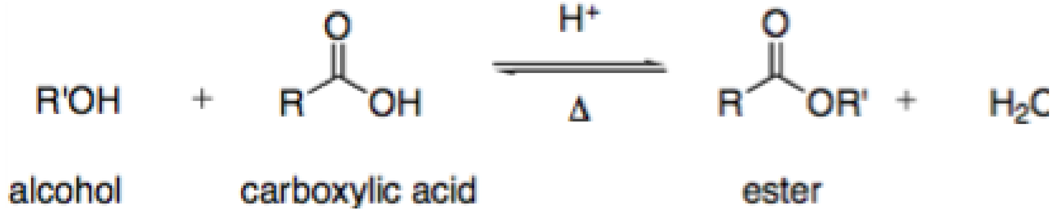
$$R_2O + 2\,H_2 \rightarrow H_2O + 2\,RH$$

Hydrocracking





Esterification

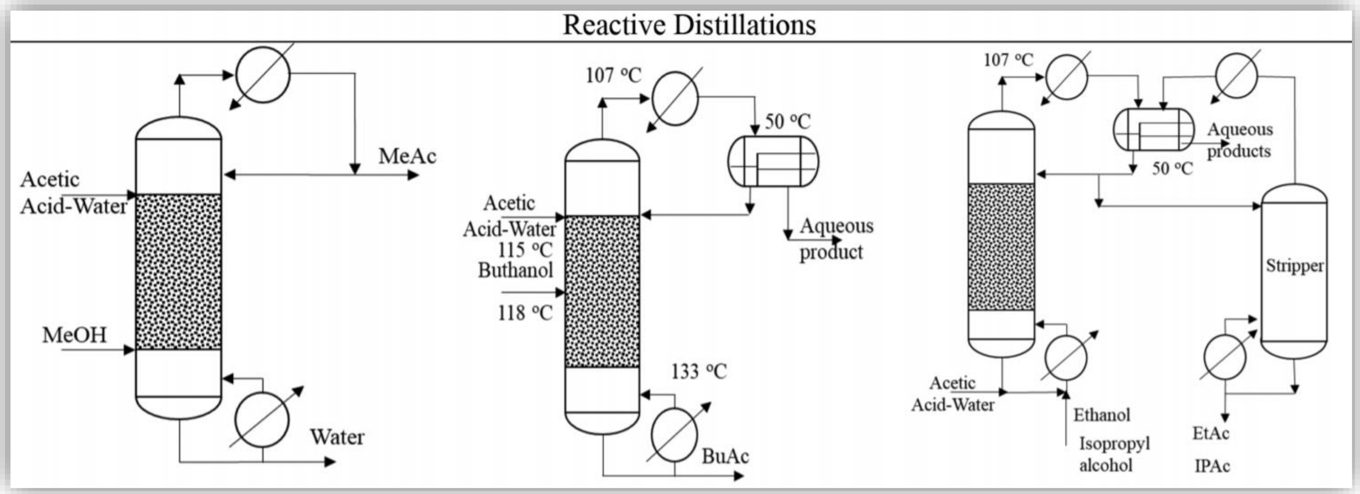


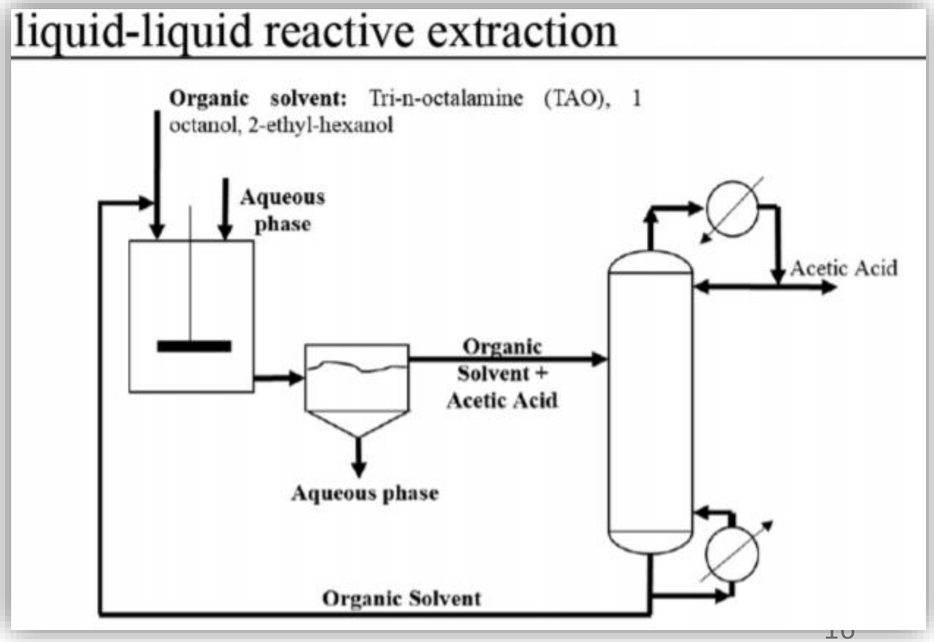
[1] Pham TN, Sooknoi T, Crossley SP, Resasco DE: Ketonization of Carboxylic Acids: Mechanisms, Catalysts, and Implications for Biomass Conversion, ACS Catal. 2013, 3, 11, 2456-2473

Purification and Separation of Targeted Compounds

Acetic Acid Separation

- Neutralization (old wood distillation industry)
- Liquid-liquid reactive extraction
- Distillation(azeotropic, extractive or reactive)
- Liquid-liquid extraction





Purification and Separation of Targeted Compounds

Hydroxyacetaldehyde (glycolaldehyde)

- Liquid-liquid extraction with ionic liquids
- Rotary evaporator and cooler
- Reactive extraction with primary amine Primene JM-T

Levoglucosan

- Water extraction
- Simultaneous esterification and acetylation with online solvent extraction (SEAWOSE) in butanol
- Distillation (steam, fractional vacuum, vacuum) followed by liquid liquid extraction
- Solid-liquid extraction

Bio-oil Refinery Conceptual Frame

Bio-oil → **Fractionation** → **Reaction** → **Purification** → **Products**

Bio-oil

- A Water
- B Methanol
- C Acetol
- D HHA
- E Acetic Acid
- F Mono-phenols
- G Levoglucosan
- H Large sugar
- I Pyrolytic humins
- J Pyrolytic Lignins
- K Hybrid Oligomers

Fractionation

- F1 Single step condensation
- F2 Fractional condensation
- F3 Conventional Distillation
- F4 Reactive distillation
- F5 Molecular distillation
- F6 Water extraction
- F7 Solvent extraction
- F8 Temperature swing extraction
- F9 Super-critical CO_2 extraction
- F10 Solid-liquid extraction
- F11 Nano-filtration
- F12 Pervaporation

Reaction

- R1 Hydrogenation
- R2 Hydrocracking
- R3 Hydrodeoxygenation
- R4 Esterification
- R5 Alkylation
- R6 Aldol Condensation

Purification

Acetic Acid

- P1 Precipitation with lime
- P2 LLE with fatty acids
- P3 Azeotropic distillation
- P4 Extractive distillation
- P5 Liquid-liquid reactive distillation
- P6 Reactive Distillations

Acetol

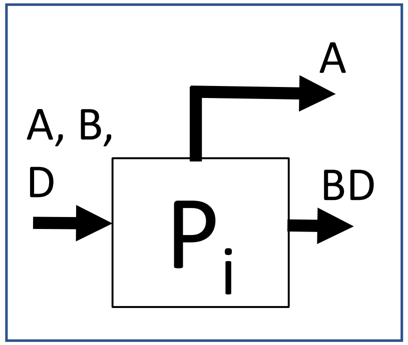
- P7 Acid resin
- P8 Liquid liquid extraction with ionic liquids

Hydroxyacetaldehyde

- P9 Evaporation and cooling
- P10 Reactive straction

Products

???



Products

Bio-oil Cost: Close to $ 150 t^{-1}

- **Fuels (gasoline): $ 600-700 t^{-1}**
- **Charcoal: $ 500 t^{-1}**
- **Light olefins** (ethylene, propylene, butadiene): **$ 900-1,500 t^{-1}** used for plastic production.
- **Small Oxygenated molecules:**
  - Methanol, ethanol, formic acid and acetic acid: **$ 400-770 t^{-1}**
  - Acetone, butanol, ethylene glycol, propylene glycol: **$ 1,100-1,800 t^{-1}** ←
- **Polymers:**
  - Polyester, polyurethane: **less than $ 1,000 t^{-1}**
  - Polyamide, polypropylene, polyether-polyols and hot melt adhesive: **over $ 1,000 t^{-1}**
- **Carbon fiber**: high market value: **more than $ 50,000 t^{-1}** ←
- **Agriculture chemicals** Glyphosate: **$4,000 - $6,000 t^{-1}** , Raw wood vinegar (aqueous phase from pyrolysis oils): **$600 t^{-1}** (Asia) ←

We need to develop chemicals for agriculture

Oxygenated products are desired to increase product yield

Bioproducts

C1-C4: Acetone | Methanol | Isopropanol | HHA | Acetic Acid | Olefins | Biogas | Food Additives | Biolime

Monophenols: Alkylated phenols | Resins and Adhesives | Pesticides and wood preservatives | BTXs | Fuels

Anhydrosugars: Polyethers | Ethanol | Butanol | Surfactants | Furans | Biogas

Pyrolytic humins: Semi-ductile thermoset | Slow release fertilizers | Bio-carbon electrodes | Carbon Fibers | Biogas

Pyrolytic lignins: Asphalt Paving Substitution | Antioxidants | Bio-carbon electrodes | Carbon Fibers | Fuels

Bio-oil Refinery Conceptual Frame

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- F8 Temperature swing extraction
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- F10 Solid-liquid extraction
- F11 Nano-filtration
- F12 Pervaporation

Reaction

- R1 Hydrogenation
- R2 Hydrocracking
- R3 Hydrodeoxygenation
- R4 Esterification
- R5 Alkylation
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Purification

Acetic Acid

- P1 Precipitation with lime
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Acetol

- P7 Acid resin
- P8 Liquid liquid extraction with ionic liquids

Hydroxyacetaldehyde

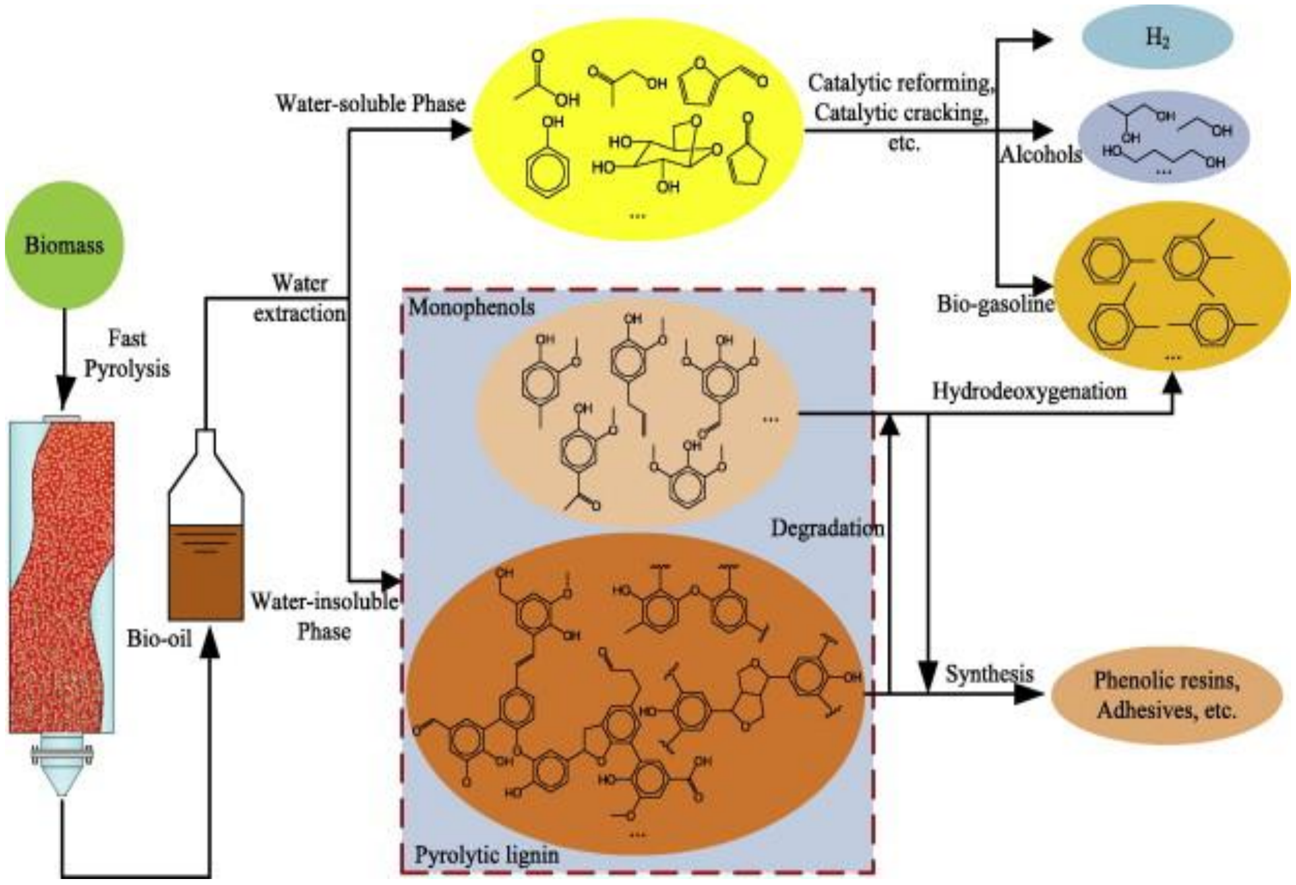
- P9 Evaporation and cooling
- P10 Reactive straction

Products

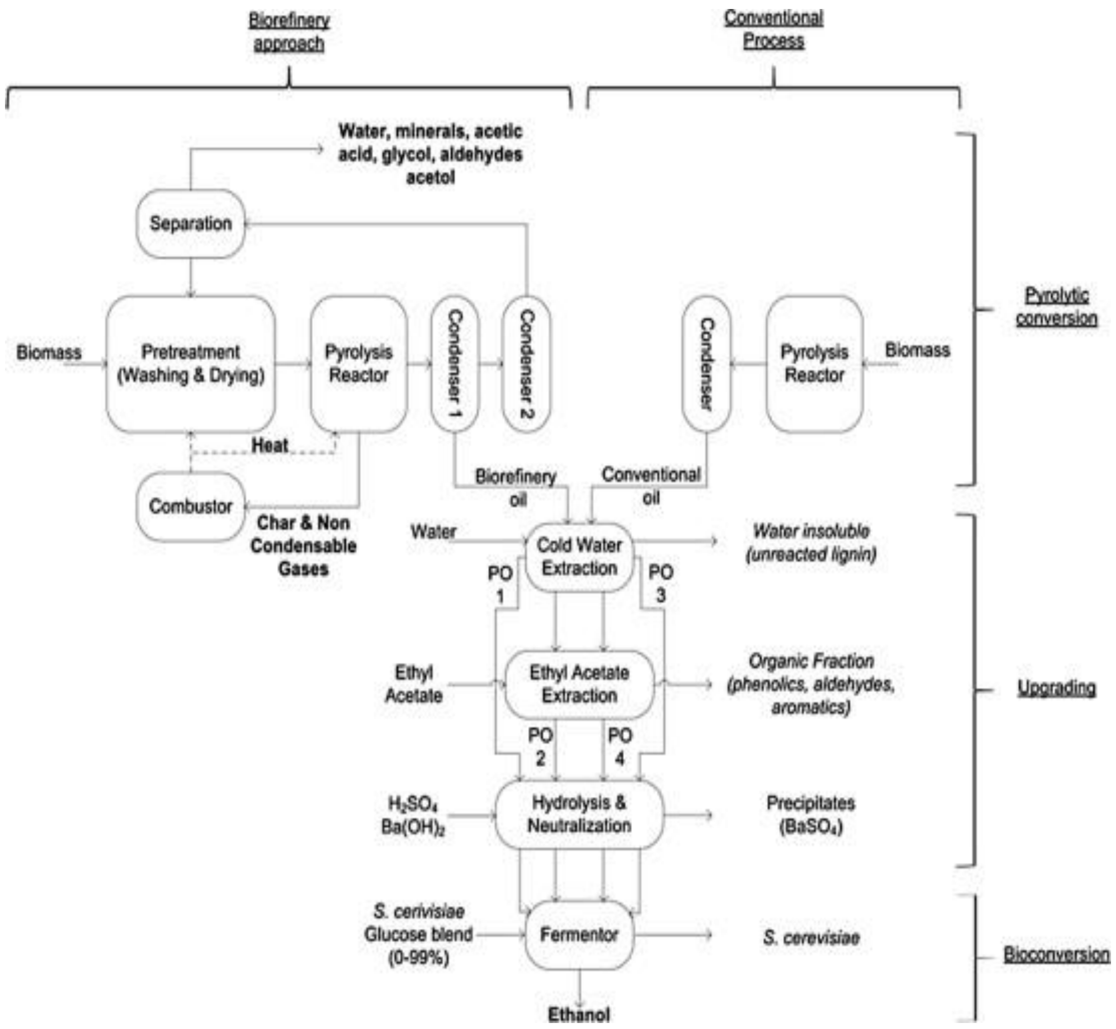
- L Fuel oil
- M Transportation fuels
- N Pesticides
- O Wood preservatives
- P Slow release fertilizers
- Q Asphalt Paving
- R Resins and Adhesives
- S Carbon fiber
- T Olefins
- U Food additives
- V Polyethers
- W Carbon electrodes
- X Sufactants

Bio-oil Refinery

Shurong Wang's group bio-refinery concept (Wang et al 2014)



Kersten's group bio-refinery concept (Luque et al 2014)

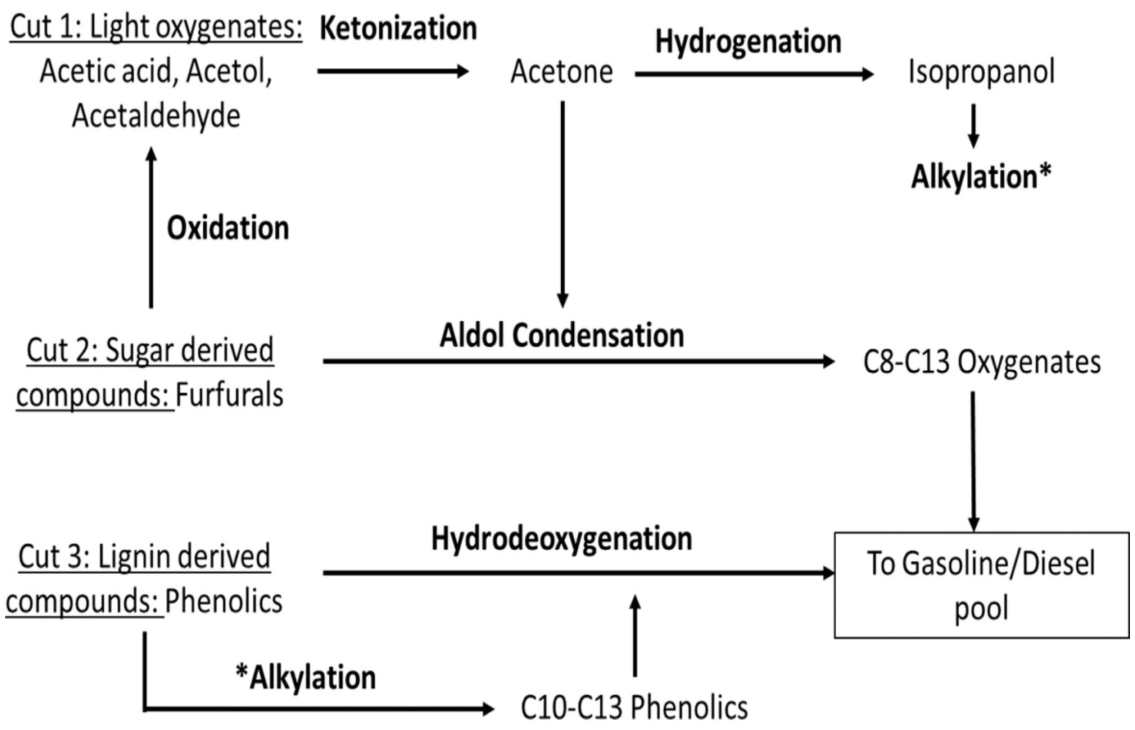


Wang, S.; Wang, Y.; Cai, Q.; Wang, X.; Jin, H.; Luo, Z. Multi-step separation of monophenols and pyrolytic lignins from the water-insoluble phase of bio-oil. *Sep. Purif. Technol.* 2014, *122* (10), 248– 255,

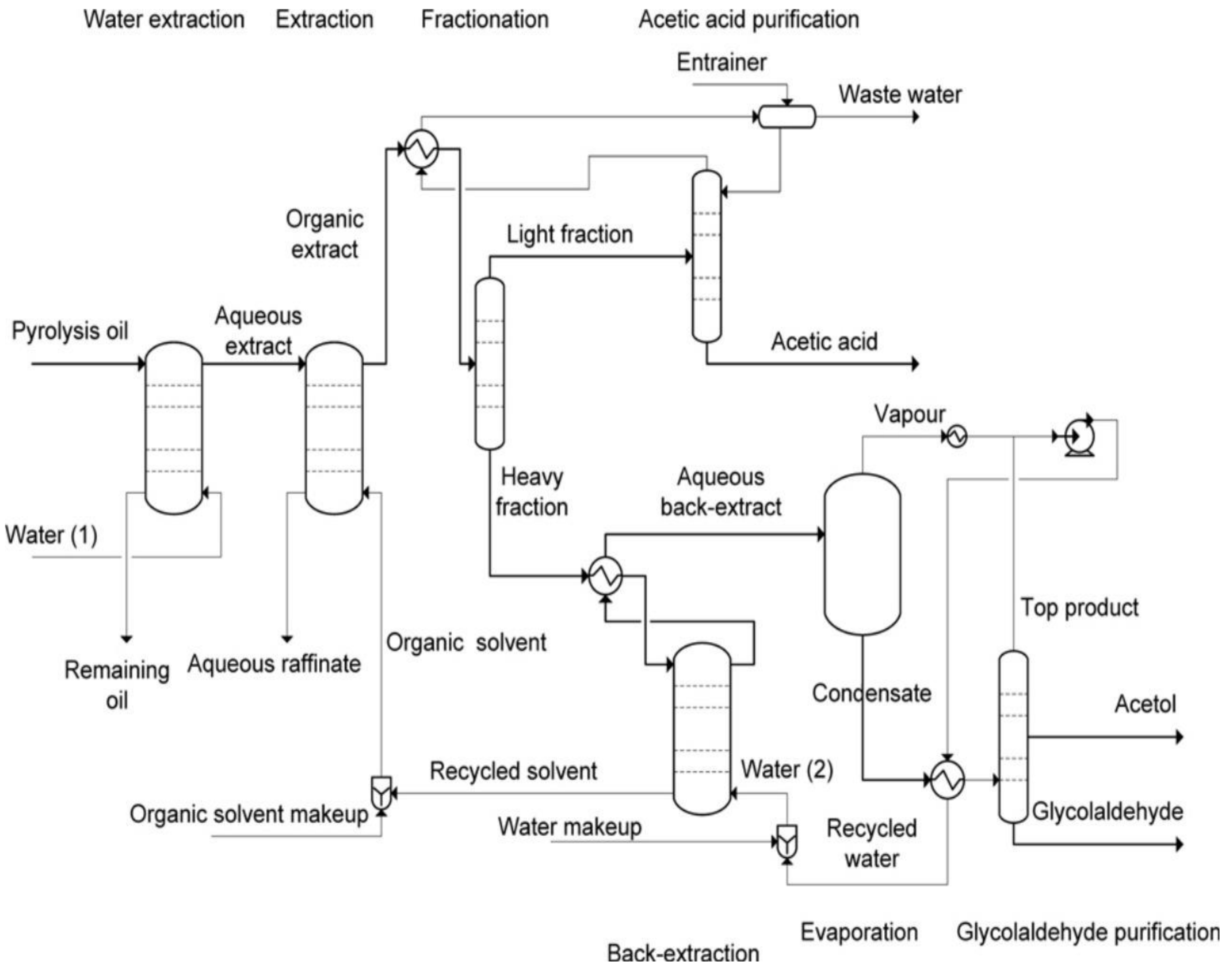
Luque, L.; Westerhof, R.; Van Rossum, G.; Oudenhoven, S.; Kersten, S.; Berruti, F.; Rehmann, L. Pyrolysis based bio-refinery for the production of bioethanol from demineralized lingo-cellulosic biomass. *Bioresour. Technol.* 2014, *161*, 20– 28,

Bio-oil Refinery

Resasco's group bio-refinery concept (Phan et al 2014)



Vitasari et al bio-refinery concept (Vitasari et al 2015)



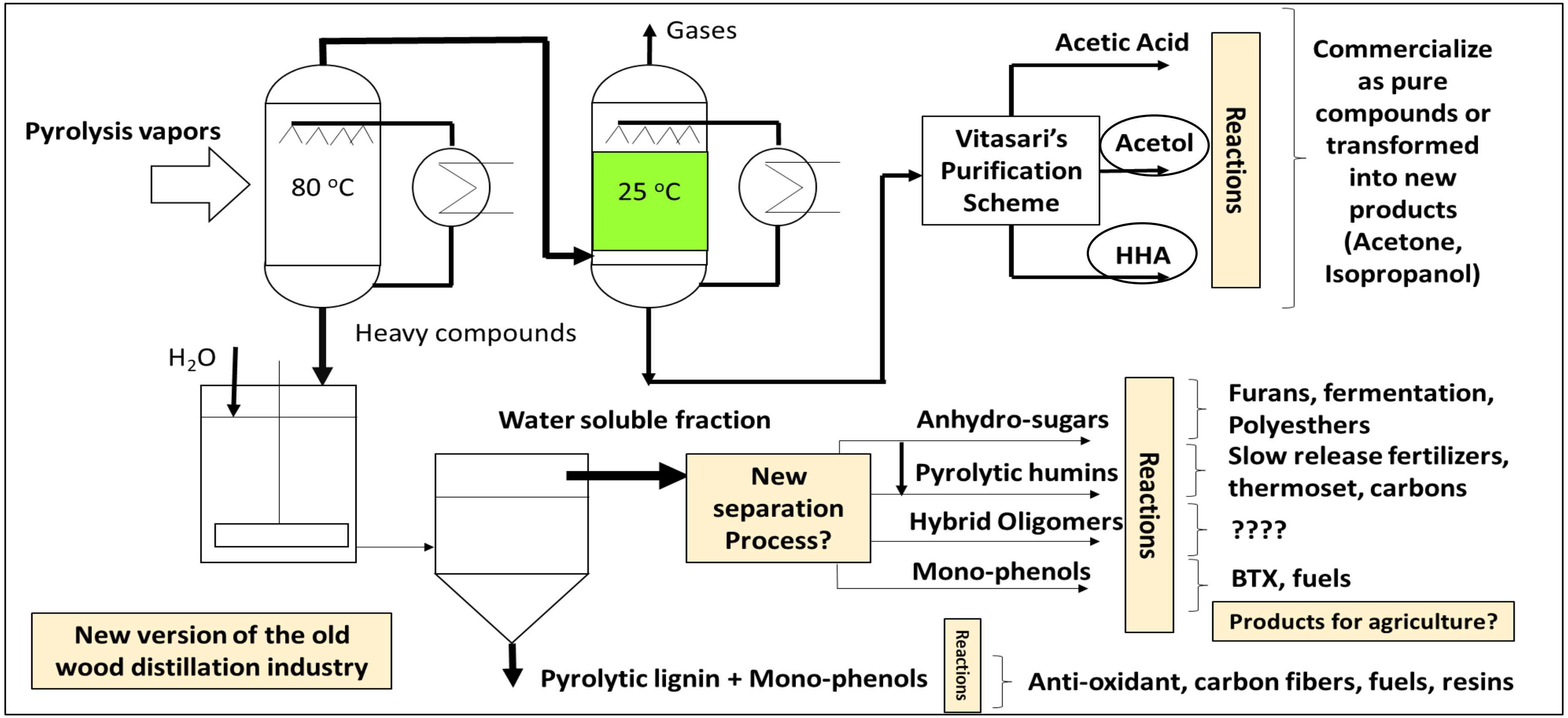
Pham, T. N.; Shi, D.; Resasco, D. E. Evaluating strategies for catalytic upgrading of pyrolysis oil in liquid phase. *Appl. Catal., B* 2014, *145*, 10– 23

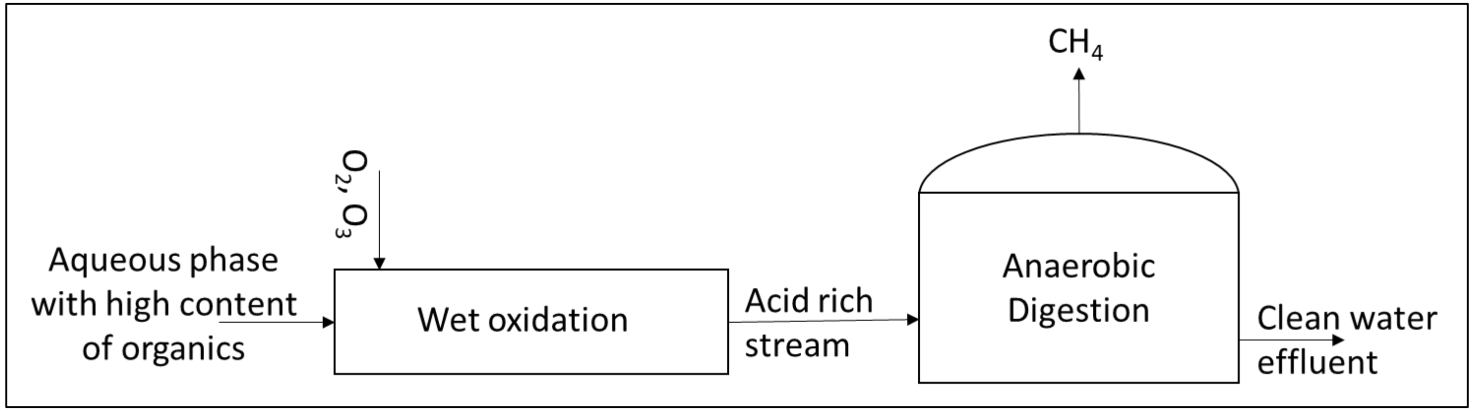
Vitasari, C. R.; Meindersma, G. W.; de Haan, A. B. Conceptual process design of an integrated bio-based acetic acid, glycolaldehyde, and acetol production in a pyrolysis oil-based biorefinery. *Chem. Eng. Res. Des.* 2015, *95*, 133– 143

Bio-oil Refinery

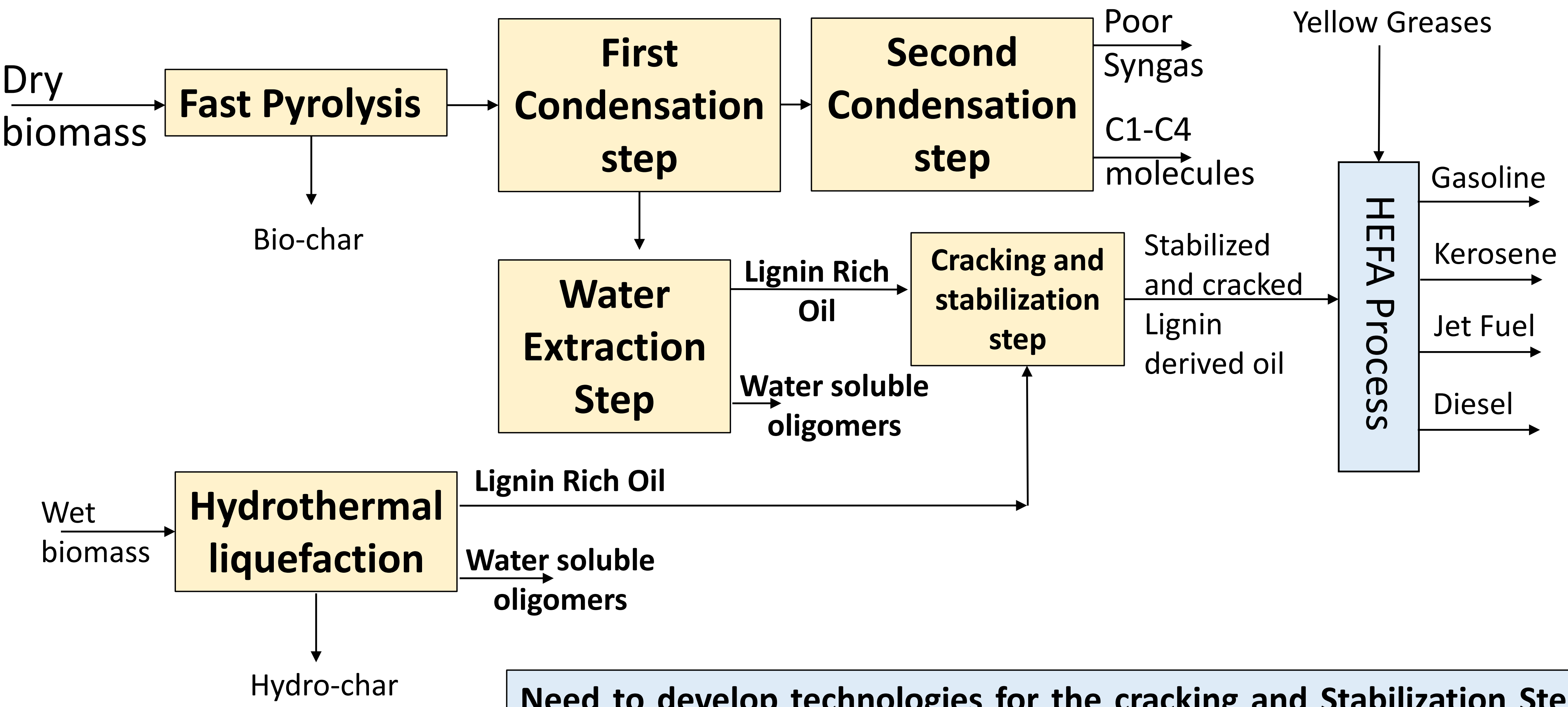
We need to make a good use of all the bio-oil fractions

Waste water treatment challenge (High content of toxic organics in aqueous effluents)





WSU-PNNL concept for co-hydrotreatment of lignin rich fraction and Yellow Greases in HEFA units



Need to develop technologies for the cracking and Stabilization Step and Standards for stabilized lignin rich oils to be used in HEFA units.

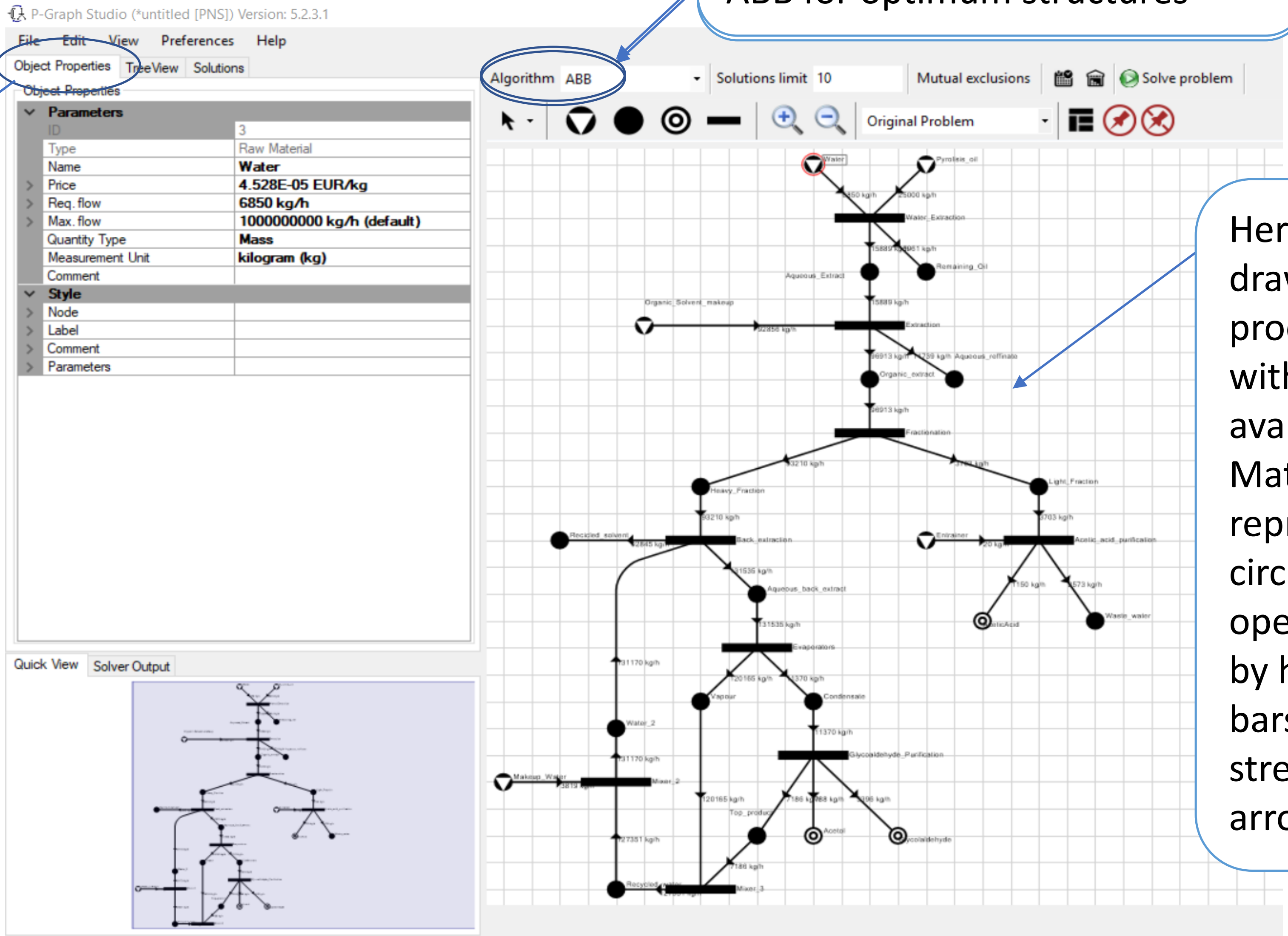
Process Graph (P-graph)

- In face of the vast number of bio-refinery possibilities, we propose the use of P-graph
- Initially developed by professors Ferenc Friedler and L. T. Fan, in the early 1990s, to represent the structure of a process synthesis
- Rigorous model-building
- Efficient identification of optimal solutions to problems involving process synthesis
- This methodology can potentially be used to **construct a robust combination of possible structures (maximal structure) of pyrolysis oil bio-refinery, and to define feasible and economically viable networks**
- Software: P-graph Studio (FREE, available for download from: p-graph.com)

P-graph Studio Interface

Select algorithm: MSG for maximal structure generation, SSG for feasible structures, and ABB for optimum structures

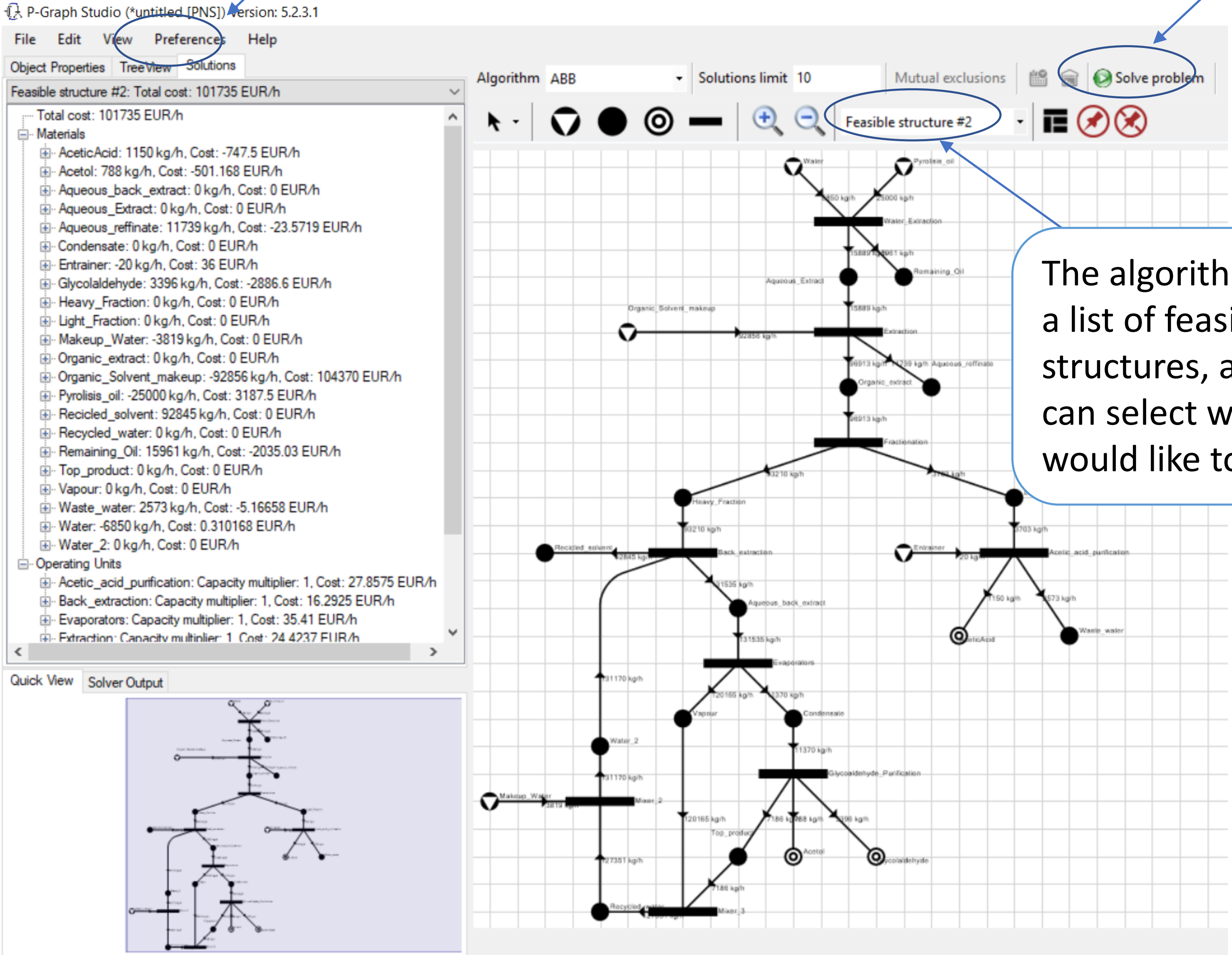
Here the user input the object (material, Operating unit or stream) properties



Here the user draws the process scheme with the available data. Materials are represented by circles, operating units by horizontal bars, and streams by the arrows.

Shows the solution of the selected structure

Run the selected algorithm



The algorithm generates a list of feasible structures, and the user can select which one they would like to display

Summary

Only two bio-oil refinery concepts thoroughly studied

Current models only focusing on the production of drop in jet fuels are unliked to be economically viable

Hundreds of new bio-oil refinery concepts can be generated based on the large number of fractionation unit operations, reaction unit operations, purification unit operations and products reported in the literature.

The WSU team is exploring the use of p-graph for the automatic synthesis of new bio-oil refinery concepts.

The WSU team published a literature review and is now building a data base compatible with p-graph to generate new bio-oil refinery concepts.

QUESTIONS?