FRACTIONATED RECOVERY OF LIGNIN PYROLYSIS PRODUCTS

A techno-economic evaluation by:
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1. Background

Climate change and depletion of fossil resources have forced humanity to rethink the way we fuel our economies. Researchers around the world are investigating numerous kinds of renewable resources that could reduce our reliance on fossil fuels, but a large portion of this research is merely aimed at the production of 'green' energy, somehow overlooking the need for new methods to produce renewable chemicals.
However, the second most abundant organic resource in the world, lignin, could prove to be key into unlocking mass production of renewable chemicals due to its aromatic molecular structure. Lignin is the only renewable source of aromatic carbon in the world, meaning that it could be used as a feedstock material for a substantial share of fossil derived chemicals. Recovery of these aromatic compounds requires degradation of the lignin macromolecule [Fig.1], one way to accomplish this is by means of fast pyrolysis.
Fast pyrolysis of lignin, i.e. rapid heating without the presence of oxygen, yields three kinds of products: pyrolysis oil, bio-char and gas.

2. Research question

What is the best technology for the fractionated recovery of pyrolysis fractions that have direct value-added applications and is also good for the environment, easily up scalable and economically feasible?

3. Applications of lignin pyrolysis products

Pyrolysis product	Additional required production steps	Products	Applications
Pyrolysis oil	As is:	Organics/water mixture	Low grade fuel
	Extraction:	Alkyl phenols	Fuel additives, polymers, phenolic resins, flame retardant materials and used in the production of fragrances
		Catechols	Pesticides, fine chemicals (perfumes and pharmaceuticals)
		Guaiacols	Fine chemicals, flavorings (liquid smoke) and pharmaceuticals
		Syringols	Fragrances (liquid smoke) and resins
	Catalytic upgrading	Benzene, toluene, xylene and various other hydrocarbons	Chemicals or biofuels
	Water removal:	Dry bio-oil	Bio asphalt, solid fuel, liquid fuel, resins and carbon fibers
Lignin biochar	As is:		Solid fuel
	After treatment:		Soil improvers, activated carbon and replacement for sand in fluidized bed pyrolysis reactor
Gas	As is:		Combustion

Tab. [1] Value-added applications for lignin pyrolysis products

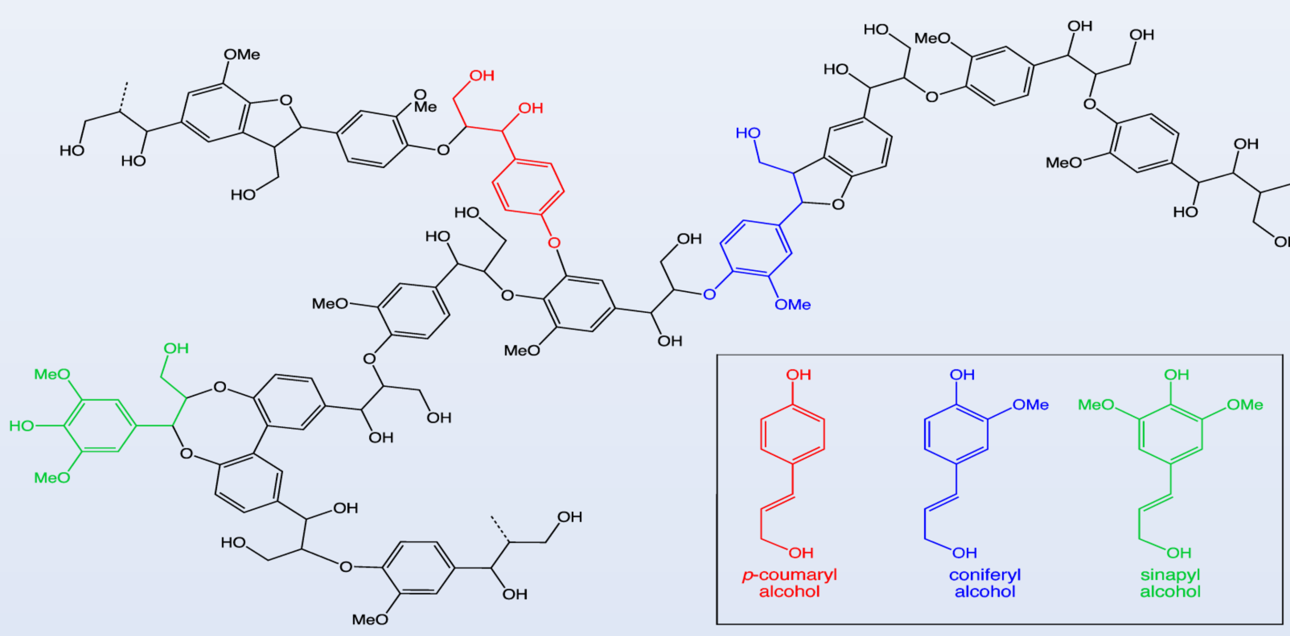

Fig. [1] Example of a lignin macromolecule and three of its primary constituents

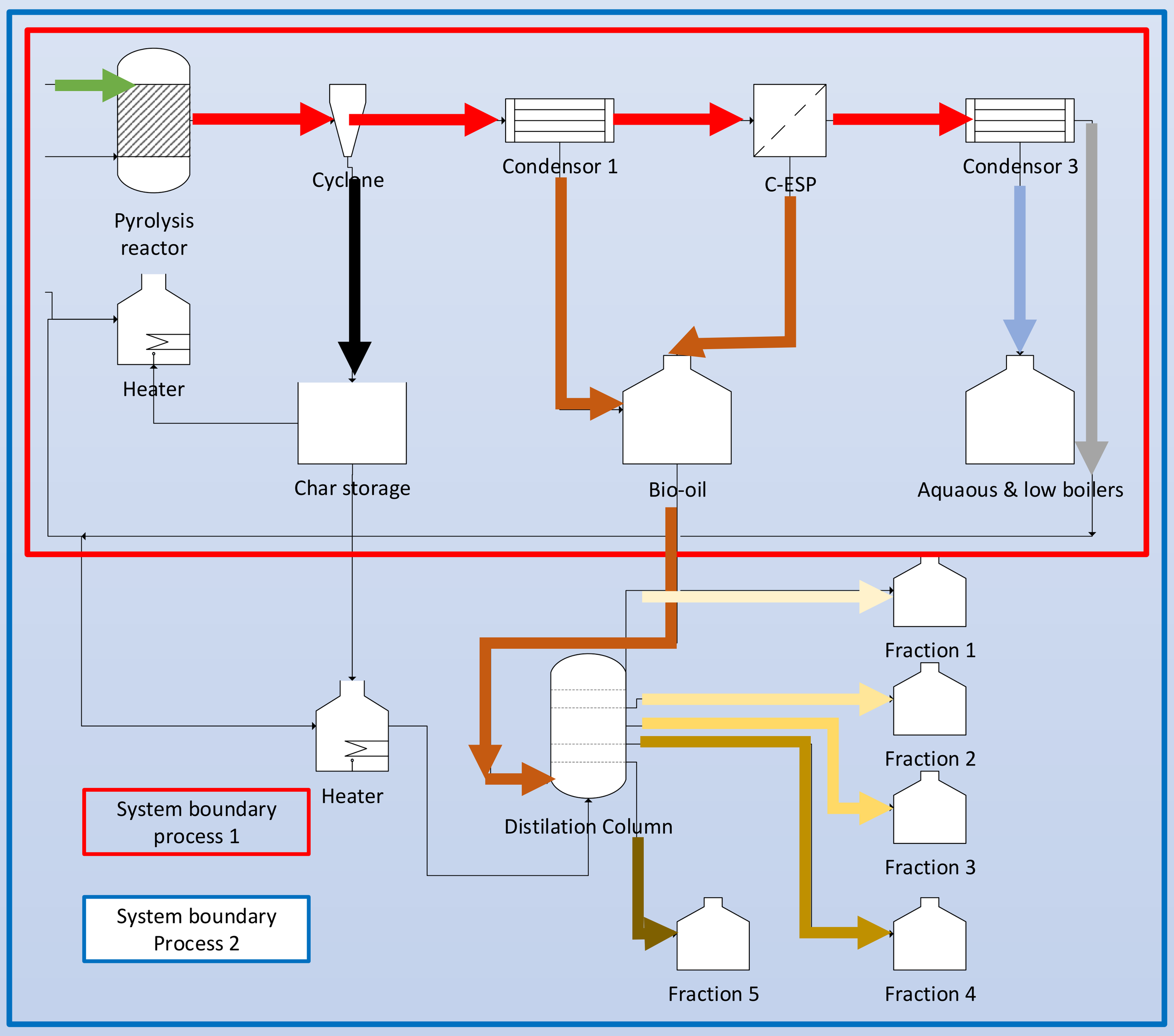

Fig. [2] Proposed system for the fractionated recovery of lignin pyrolysis products

- Powdered lignin feedstock material
- Non-condensable gasses
- Hot pyrolysis vapors
- Top fraction distilled bio-oil
- Bio-char
- Middle fractions distilled bio-oil
- Dry phenolic lignin pyrolysis oil
- Bottom fraction distilled bio-oil
- Low boilers and water

Lignin bio-oil compounds	Price ($/kg)	Lignin bio-oil compounds	Price ($/kg)
Catechols:	**5**	**Syringols:**	**7**
3-Methoxypyrocatechol	5	2,6-Dimethoxyphenol	25
Pyrocatechol	5	4-(2-propenyl) syringone	5
		4-Methylsyringol	5
Alkyl phenols:	**3**	Acetosyringone	10
4-Ethylphenol	1,2	Syringaldehyde	1
Phenol	3		
O-cresol	5	**Light ends:**	**0,05**
P-cresol	3	Acetone	0,01
M-cresol	5	Methanol	0,01
		Acetic acid	0,2
Guaiacols:	**6**	2-Furaldehyde	10
2-Methoxyphenol	3		
2-methoxy-4-vinyl-phenol	3	**Water**	
4-Ethylguaiacol	5		
4-Methylguaiacol	3	**Unidentified monomers**	**1**
Aceto-vanillone	25		
Isoeugenol	25	**Unidentified oligomers**	**0,3**
Vanillin	25		
Source: Alibaba, Sigma-Aldrich			

Tab.[2] Estimated selling value of LPO constituents ($/kg)

4. Process description [Fig.2]

Process 1: Fractional condensation of hot pyrolysis vapors
Primary product: Dry phenolic pyrolysis oil

Process 2: Fractional atmospheric distillation of dry phenolic pyrolysis oil
Primary product: Five separate fractions of structurally similar phenolic compounds

5. Economic evaluation

Outcome process 1:
Currently unfeasible. Production of dry lignin pyrolysis oil (LPO) would require a breakeven price of at least $1.25/kg without subsidies, and $0,97/kg with potential subsidies. Dry LPO has a similar burning value to bio-ethanol, which is priced at $0,79/kg, making this process to expensive to produce fuel. Further research into possible applications of a phenolic oil mixture are required to determine whether this process is feasible for the production of renewable chemicals.

Outcome process 2:
Currently unfeasible. The expected selling price of the five separate phenolic fractions was too low to justify large scale production [Tab.2]. The process was modelled using three types of lignin feedstock material, and resulted in (minor) losses for each type. The feasibility of the second process could improve in the near future if subsidies become available for development of renewable chemical production processes.

Pro-Forma Income Statement 7000 hours

Fast pyrolysis of lignin with fractional distillation of the condensed dry LPO

	Wheat straw OS	Granit	Alcell
REVENUE			
Gross sales	$5.825.111	$8.705.121	$7.467.574
Net Sales	$5.825.111	$8.705.121	$7.467.574
OPERATING EXPENSES			
Fixed			
Salaries and wages	$970.000	$970.000	$970.000
Maintenance	924.000	924.000	924.000
R&D	470.076	470.076	470.076
Depreciation	513.333	513.333	513.333
Overhead	616.000	616.000	616.000
Total Fixed Operating Expenses	$3.493.409	$3.493.409	$3.493.409
Variable Operating Expenses			
Costs of raw material	$5.250.000	$5.250.000	$5.250.000
Utilities	658.106	658.106	658.106
Total Variable Operating Expenses	$5.908.106	$5.908.106	$5.908.106
Total Operating Expenses	$9.401.515	$9.401.515	$9.401.515
Net Income Before Taxes	($3.576.404)	($696.394)	($1.933.941)
Taxes on income	0	0	0
Net Income After Taxes	($3.576.404)	($696.394)	($1.933.941)
Extraordinary gain or loss	$0	$0	$0
Income tax on extraordinary gain	0	0	0
NET INCOME (LOSS)	($3.576.404)	($696.394)	($1.933.941)

Fig. [3] Expected annual income statement process 2

6. Conclusion & Recommendations

It is advised against large-scale implementation of the proposed processes. Under current market conditions neither of the processes show satisfactory results in terms of economic viability. However, taking into account the relative minor structural losses incurred by the processes, it is expected that the production of renewable aromatic chemicals from lignin will attain feasibility in the near future. To achieve this several issues are in need of addressing:

- Lignin feedstock material is currently too expensive and of insufficient quality. In order to reduce the price and improve the quality of lignin, companies that produce lignin must rethink their production process and integrate lignin as a value-adding compound as opposed to a waste product.
- A lack of research into the possible applications of a phenolic bio-oil mixture and lignin bio-char make it challenging to accurately determine their value. Researchers and (petro)chemical companies must work together to find a suitable use for this mixture.
- Researchers need to better understand lignin reaction kinetics, as this will help control the reaction and the formation of desired end products.