Techno-Economic Analysis of Lignin First Approach

Biomass has three main components, cellulose, hemicellulose and lignin. The cellulose and hemicellulose are extracted and converted into biofuels with the help of specific enzymes. This industry is growing and is well established. However, if we look into these industries, they extract out the lignin in the last stage, which is highly condensed and hence difficult to make any use of it, so eventually it is just burnt.

In the recent years, there has been growing research on lignin first extraction approach. The main focus is on lignocellulose biomass which are basically wastes. Lignin is a complex aromatic polymer made up of several monomers (Discussed later), and these aromatic monomers are useful in making perfumes, inks, adhesives, etc.

The main idea behind "lignin first" is extracting the lignin, then splitting it to its monomers, and then preventing condensation of the monomers. There are several ways to start this process, one way is by reductive catalytic fractionation (RCF), and one more is by using protection group chemistry.

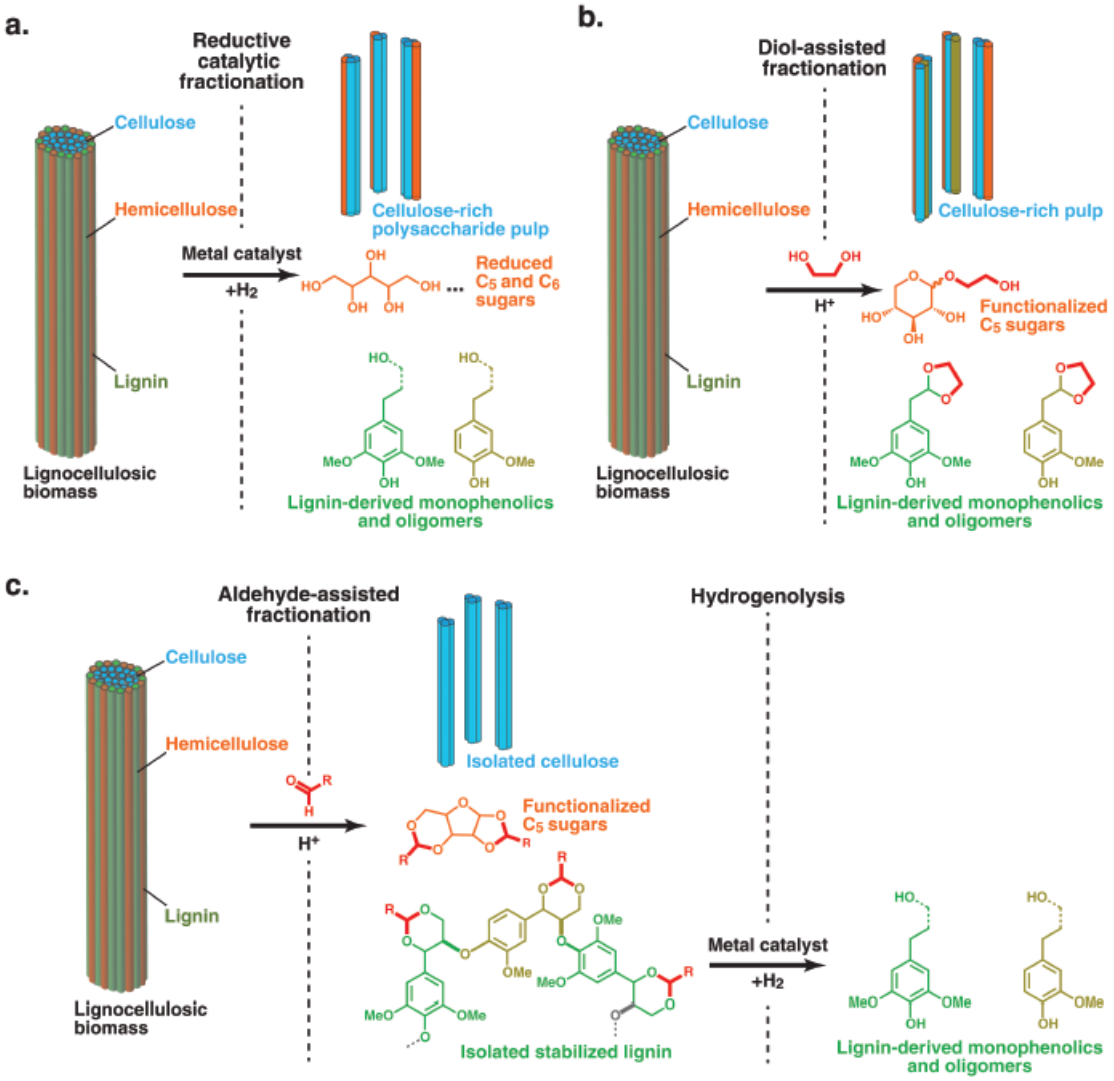
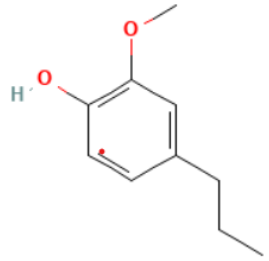


Figure 1: a-RCF b,c- Protection group chemistry

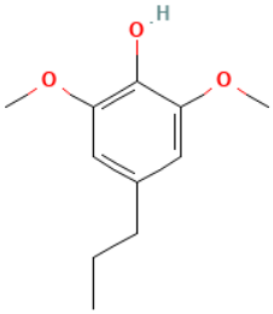
Lignin

Lignin is a complex polymer and its constituents differ for different biomass. The components that are usually present in lignin are

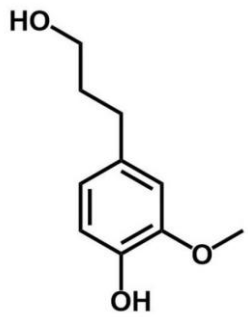
1. 4- propyl guaiacol



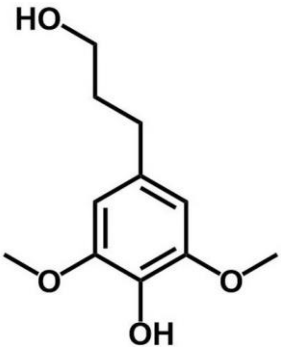
2. 4- propyl syringol



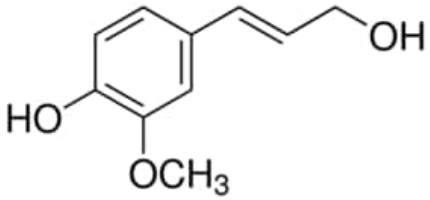
3. 4- propanol guaiacol



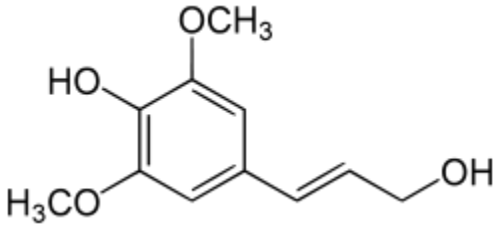
4. 4- propanol syringol



5. Coniferyl alcohol



6. Sinapyl alcohol

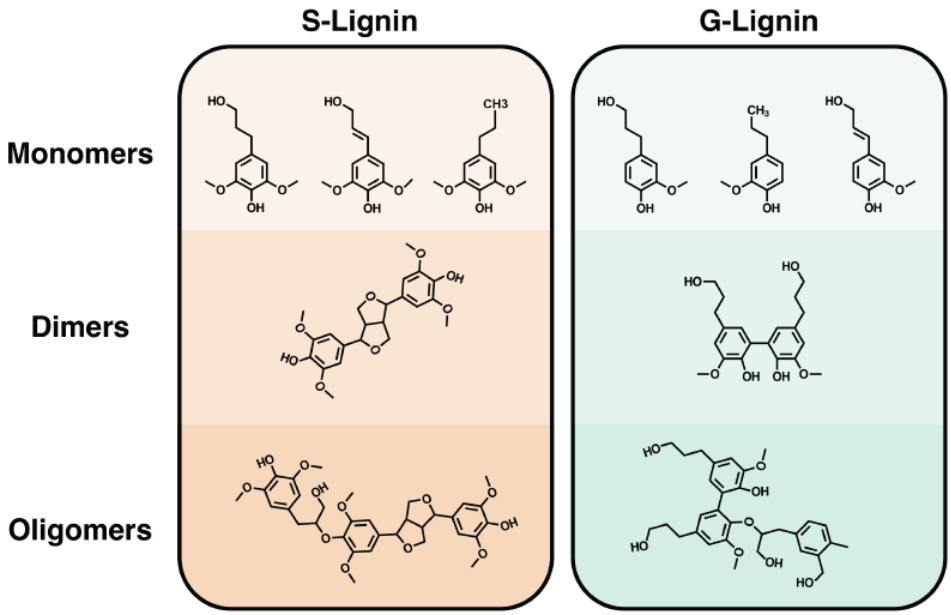


The table below shows that different biomass has different monomer composition.

Table S4 Overview of the lignin monomer distribution, the total Klason lignin content, the extractives and the amount of C6 and C5 sugars for birch, poplar, softwood and miscanthus.

	Monomer products[a]			Lignin oil[b]			Klason lignin (wt%)	Extractives (wt%)	C6-sugar (C%)	C5-sugar (C%)
Substrate	%H	%G	%S	%H	%G	%S				
Birch	0	23	77	0	26	74	19.1	2.5	39.3	20.7
Poplar	0	37	63	0	45	55	21.2	4.2	44.0	14.7
Softwood[c]	0	96	4	0	98	2	27.0	4.5	53.8	6.1
Miscanthus	27	47	25	14	61	25	24.3	1.8	39.1	22.1

[a] Distribution of the monomer building blocks in the monomer product fraction after protolignin hydrogenolysis. [b] Distribution of the monomer building blocks in the lignin oil, determined with 2D HSQC-NMR as described in the procedure section. [c] The traces of S-units in the softwood sample likely originate from hardwood impurities.



Lignin can be obtained from various sources, hardwood, softwood, and grasses. It has been observed that hardwood produce the highest lignin oil and high syringol content. The reason for this is due to less carbon-carbon linkage in hardwoods.

*Note: A higher S-content relates to higher monomer yields and better delignification.

There are dimers and oligomers also formed during the process, we have referred these from a paper[1].

Simulation

Reference paper: "Techno-economic analysis and life cycle assessment of a biorefinery utilizing reductive catalytic fractionation"

As the paper describes we'll be looking into RCF of Lignin. Software used for simulation is ASPEN. *Currently, the material flow simulation is performed.*

Challenges:

1. The lignin compounds must be user-defined and no details have been given in the paper.
2. The exact process flowsheet has not been given in the paper.
3. Problems with the recycle stream in ASPEN
4. How to represent Cellulose, Hemicellulose and Lignin in ASPEN?
5. How to account for mass balance in case of lignin splitting to its monomers?
6. How to account for the CO_2 and CO produced?

Steps and assumptions taken to overcome these challenges.

In case of compounds that are not present in ASPEN database, ASPEN allows creating compounds. Only 4-propyl guaiacol is present in the database, the rest has been user defined and their properties have been estimated through the NIST Engine available in ASPEN. The properties for cellulose, xylan, lignin were referred from a paper[3]

Flowsheet problem: In the paper the exact flow diagram has not been given, so the unit processes are inserted according to the desired output.

Recycle stream problem: In ASPEN there is a thumb rule, to always add a purge in the recycle stream. This is done mainly to prevent the accumulation of the non-reacting components.

Representing Cellulose, Hemicellulose and Lignin in ASPEN: Paper referred "*Development of an ASPEN PLUS Physical Property Database for Biofuels Component*"

Glucose formula : $C_6H_{12}O_6$

Cellulose formula: $C_6H_{10}O_5$

Explanation: Cellulose is mainly a polymer of glucose molecules. Hence when two glucose polymerizes, it results in cellulose with the elimination of a water molecule, hence the above formula of cellulose. Similar treatment is done to galactose, mannose for galactan and mannan. In case of xylan and arabinan, xylose is considered as the monomer and again elimination of a water molecule results in xylan.

Coming to Lignin, it is difficult to come up with one monomer. However in a paper they have used vanillin as the monomer. Reason for using vanillin is because it has similar heating capacity with the biomass used. Hence, the simulation was carried forward using vanillin as the monomer for Lignin.

How to account for the mass balance for Lignin splitting?

$10C_8H_8O_3 + 30H_2$ --------> $8C_{10}H_{14}O_2 + 14H_2O$

Above is the idea used behind the mass balance. Water was assumed to given out as the product as well, to balance the reaction. Similar steps were followed for the other monomers, dimers and oligomers.

How to account for CO_2 and CO produced?

In the paper it was given that there was 5% solvent loss to carbonaceous gases. So the following reaction scheme was followed

CH_3OH ----------> $CO + H_2O$

$CH_3OH + CO$ ----------> CH_3COOH

CH_3COOH ----------> $CO_2 + CH_4$

The above scheme reference was from: https://www.intechopen.com/chapters/65202

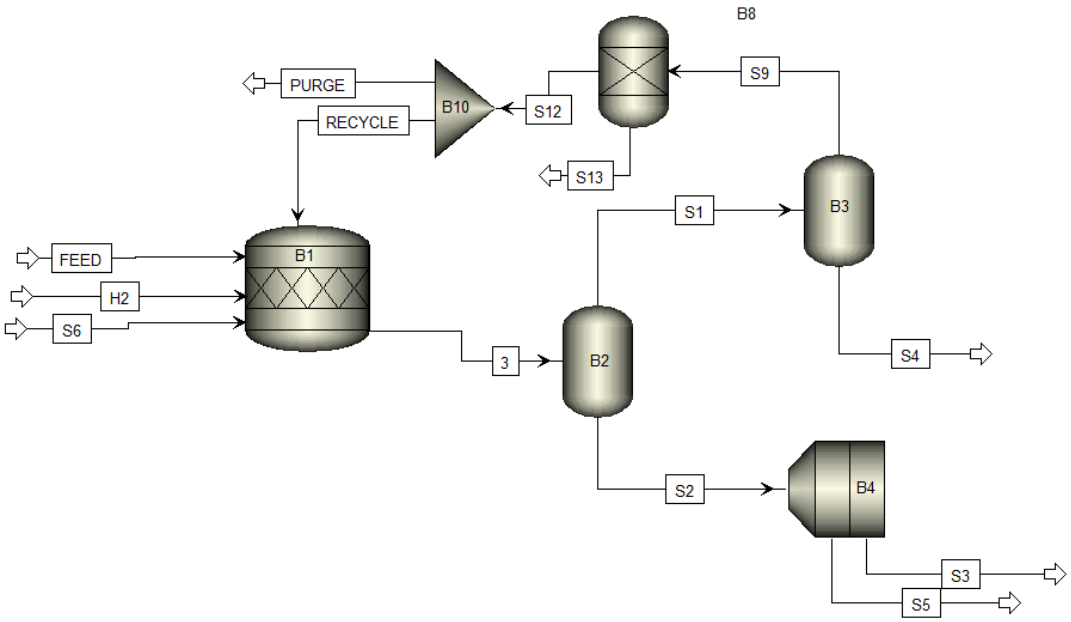
$$CH_3COOH \rightarrow CH_4 + CO_2$$

$$2C_2H_5OH + CO_2 \rightarrow CH_4 + 2CH_3COOH$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

However, in the given paper there were no CH_4 involved. So, more study has to be done on this.

*As a reference, an ASPEN file of bioethanol production was made available at NREL website.



Under Progress

Currently, I'm simulating the entire RCF process with the above data discussed. The simulation is running fine, but I haven't compared with the paper. Next I will try to match the results obtained in the literature .

Stream S3- Lignin Oil product
Stream S5- Carbohydrate pulp.
Flowsheet is not complete, methanol recycle has to be added.
Recycle stream contains only H_2, purge is 3.1%

Table 1: Reactor inlets and outlets

		3(Outlet)	FEED	H2	S6
Mass Flows	**kg/hr**	**942359.2172**	**105000**	**450**	**767400**
DIMERG	kg/hr	857.9180257	0	0	0
DIMERS	kg/hr	1375.552726	0	0	0
OLIGOG	kg/hr	631.2984009	0	0	0
OLIGOS	kg/hr	1057.292174	0	0	0
GUAICOL	kg/hr	1794.573005	0	0	0
PROLG	kg/hr	679.5245455	0	0	0
PROLS	kg/hr	844.1692205	0	0	0
DEXTR-01	kg/hr	4339.954818	0	0	0
D-ARA-01	kg/hr	114.5442685	0	0	0
MANNO-01	kg/hr	1726.648691	0	0	0
XYLOS-01	kg/hr	895.3543654	0	0	0
D-GAL-01	kg/hr	653.3265318	0	0	0
WATER	kg/hr	103090.7155	26208	0	76740
HYDRO-01	kg/hr	71810.26906	0	450	0
METHA-01	kg/hr	656558.6625	0	0	690660
CELLULOS	kg/hr	35154	39060	0	0
GALACTAN	kg/hr	588	1176	0	0
MANAN	kg/hr	1554	3108	0	0
ARIBAN	kg/hr	67.2	168	0	0
XYLAN	kg/hr	10468.08	11256	0	0
LIGNIN	kg/hr	7207.2	24024	0	0
LIGSOL	kg/hr	5690.313013	0	0	0
SYRINGOL	kg/hr	3271.869966	0	0	0
CARBO-01	kg/hr	18498.07457	0	0	0
CARBO-02	kg/hr	377.3478221	0	0	0
ACETI-01	kg/hr	6310.280512	0	0	0
METHANE	kg/hr	6743.047476	0	0	0

Feed Composition (Wet basis)

Biomass used was Poplar
Temperature: 25C, Pressure: 1bar, Flow rate = 105000kg/hr (according to paper)

Conditions of other streams and reactor, and also compositions of monomers, dimers and oligomers were taken from the table below.

WATER	0.2496
HYDRO-01	
METHA-01	
CELLULOS	0.372
GALACTAN	0.0112
MANAN	0.0296
ARIBAN	0.0016
XYLAN	0.1072
LIGNIN	0.2288

	Methanol	Ethanol	Hydrogen-free	Ethylene glycol
RCF reactor solvent (volumetric ratio)	9 : 1 methanol : water	85 : 15 ethanol : water	1 : 1 ethanol : water	99 : 1 ethylene glycol : water
Solvent loading (L per dry kg biomass feed)	9	9	9	9
Hydrogen loading (L_{STP} per min per dry kg biomass)	10	10	0	10
RCF reactor temperature (°C)	200	200	210	200
RCF reactor pressure (bar)	60	50	30	6
RCF reactor residence time (h)	3	3	2	3
Catalyst	15 wt% Ni/C	5 wt% Pd/C	5 wt% Pd/C	15 wt% Ni/C
Biomass delignification (wt%)	70%	60%	75%	70%
Solubilized lignin composition (wt%)				
Monomers	50%	50%	20%	50%
Dimers	25%	25%	60%	25%
Oligomers	25%	25%	20%	25%
S-Monomer composition (wt%)				
4-Propylsyringol	75%	20%	75%	75%
Dihydrosinapyl alcohol	25%	80%	25%	25%
G-Monomer composition (wt%)				
4-Propylguaiacol	66%	5%	66%	66%
Dihydroconiferyl alcohol	34%	95%	34%	34%
Carbohydrate retention (wt%)				
Cellulose	90%	95%	97%	90%
Xylan	93%	70%	38%	93%
Arabinan	40%	70%	38%	40%
Galactan	50%	70%	38%	50%
Mannan	50%	70%	38%	50%
Alcohol reforming to gases (wt% of alcohols)	0.50%	0.50%	0.50%	0.50%

Reactions

Reactions

Rxn No.	Specification type	Molar extent	Units	Fractional conversion	Fractional Conversion of Component	Stoichiometry
1	Frac. conversion		kmol/hr	0.1	CELLULOS	CELLULOS + WATER --> DEXTR-01(MIXED)
2	Frac. conversion		kmol/hr	0.5	GALACTAN	GALACTAN + WATER --> D-GAL-01(MIXED)
3	Frac. conversion		kmol/hr	0.5	MANAN	MANAN + WATER --> MANNO-01(MIXED)
4	Frac. conversion		kmol/hr	0.6	ARIBAN	ARIBAN + WATER --> D-ARA-01(MIXED)
5	Frac. conversion		kmol/hr	0.07	XYLAN	XYLAN + WATER --> XYLOS-01(MIXED)
6	Frac. conversion		kmol/hr	0.7	LIGNIN	LIGNIN --> LIGSOL(MIXED)
7	Frac. conversion		kmol/hr	0.1221	LIGSOL	10 LIGSOL + 30 HYDRO-01 --> 8 GUAICOL(MIXED) + 14 WATER(MIXED)
8	Frac. conversion		kmol/hr	0.23625	LIGSOL	11 LIGSOL + 29 HYDRO-01 --> 8 SYRINGOL(MIXED) + 9 WATER(MIXED)
9	Frac. conversion		kmol/hr	0.0629	LIGSOL	10 LIGSOL + 22 HYDRO-01 --> 8 PROLG(MIXED) + 6 WATER(MIXED)
10	Frac. conversion		kmol/hr	0.07875	LIGSOL	11 LIGSOL + 21 HYDRO-01 --> 8 PROLS(MIXED) + WATER(MIXED)
11	Frac. conversion		kmol/hr	0.0925	LIGSOL	20 LIGSOL + 36 HYDRO-01 --> 8 DIMERG(MIXED) + 12 WATER(MIXED)
12	Frac. conversion		kmol/hr	0.1575	LIGSOL	23 LIGSOL + 25 HYDRO-01 --> 8 DIMERS(MIXED) + 5 WATER(MIXED)
13	Frac. conversion		kmol/hr	0.0925	LIGSOL	31 LIGSOL + 65 HYDRO-01 --> 8 OLIGOG(MIXED) + 29 WATER(MIXED)
14	Frac. conversion		kmol/hr	0.1575	LIGSOL	34 LIGSOL + 38 HYDRO-01 --> 8 OLIGOS(MIXED) + 6 WATER(MIXED)
15	Frac. conversion		kmol/hr	0.025	METHA-01	METHA-01 --> CARBO-02(MIXED) + 2 HYDRO-01(MIXED)
16	Frac. conversion		kmol/hr	0.025	METHA-01	METHA-01 + CARBO-02 --> ACETI-01(MIXED)
17	Frac. conversion		kmol/hr	0.8	ACETI-01	ACETI-01 --> METHANE(MIXED) + CARBO-01(MIXED)

Results: (Refer to the flowsheet above)

Table 2: Outlets from reactor and centrifuge

		3(Outlet from reactor)	FEED	S3(RCF OIL)	S5(PULP)
Mass Flows	kg/hr	**942359.2172**	**105000**	**776795.4794**	**55594.42424**
DIMERG	kg/hr	857.9180257	0	857.3	0.61
DIMERS	kg/hr	1375.552726	0	1374.568962	0.98376435
OLIGOG	kg/hr	631.2984009	0	1.13E-12	8.07E-16
OLIGOS	kg/hr	1057.292174	0	1.14E-17	8.18E-21
GUAICOL	kg/hr	1794.573005	0	1793.266062	1.283421401
PROLG	kg/hr	679.5245455	0	679.0385564	0.485980655
PROLS	kg/hr	844.1692205	0	843.5652625	0.603730664
DEXTR-01	kg/hr	4339.954818	0	4336.85098	3.103838007
D-ARA-01	kg/hr	114.5442685	0	114.462339	0.081919476
MANNO-01	kg/hr	1726.648691	0	1725.413831	1.234860282
XYLOS-01	kg/hr	895.3543654	0	894.7140279	0.64033729
D-GAL-01	kg/hr	653.3265318	0	652.8592874	0.467244431
WATER	kg/hr	103090.7155	26208	102495.5583	73.3549783
HYDRO-01	kg/hr	71810.26906	0	70.14337136	0.050200863
METHA-01	kg/hr	656558.6625	0	644776.4567	461.4596355
CELLULOS	kg/hr	35154	39060	0	35154
GALACTAN	kg/hr	588	1176	0	588
MANAN	kg/hr	1554	3108	0	1554
ARIBAN	kg/hr	67.2	168	0	67.2
XYLAN	kg/hr	10468.08	11256	0	10468.08
LIGNIN	kg/hr	7207.2	24024	0	7207.2
LIGSOL	kg/hr	5690.313013	0	5686.2385	4.069580268
SYRINGOL	kg/hr	3271.869966	0	3269.470715	2.339925332
CARBO-01	kg/hr	18498.07457	0	1642.934784	1.175830908
CARBO-02	kg/hr	377.3478221	0	0.866703239	0.00062029
ACETI-01	kg/hr	6310.280512	0	6281.254093	4.495426584
METHANE	kg/hr	6743.047476	0	81.61954101	0.058414235

Carbohydrate retention 90%, and in the results, 35154 of cellulose is present in the pulp stream S5, which is 90% of 39060 cellulose present in the biomass.

Delignification is 70%

Problems: There is some error in the oligomer compounds(marked in red). Will have to check their properties. These compounds are flashing away with H_2. Properties have to be checked again.

Next Step…..

1. Fix the oligomer and dimer stream
2. Complete the methanol recycle stream
3. Match the results with that from the paper
4. Economic Analysis
5. LCA Analysis

References

1. Techno-economic analysis and life cycle assessment of a biorefinery utilizing reductive catalytic fractionation
2. Reductive lignocellulose fractionation into soluble lignin-derived phenolic monomers and dimers and processable carbohydrate pulps
3. Development of an ASPEN PLUS Physical Property Database for Biofuels Component.
4. Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol