# LIQUEFACTION OF WOOD PARTICLES BY USING PYROLYTIC OIL

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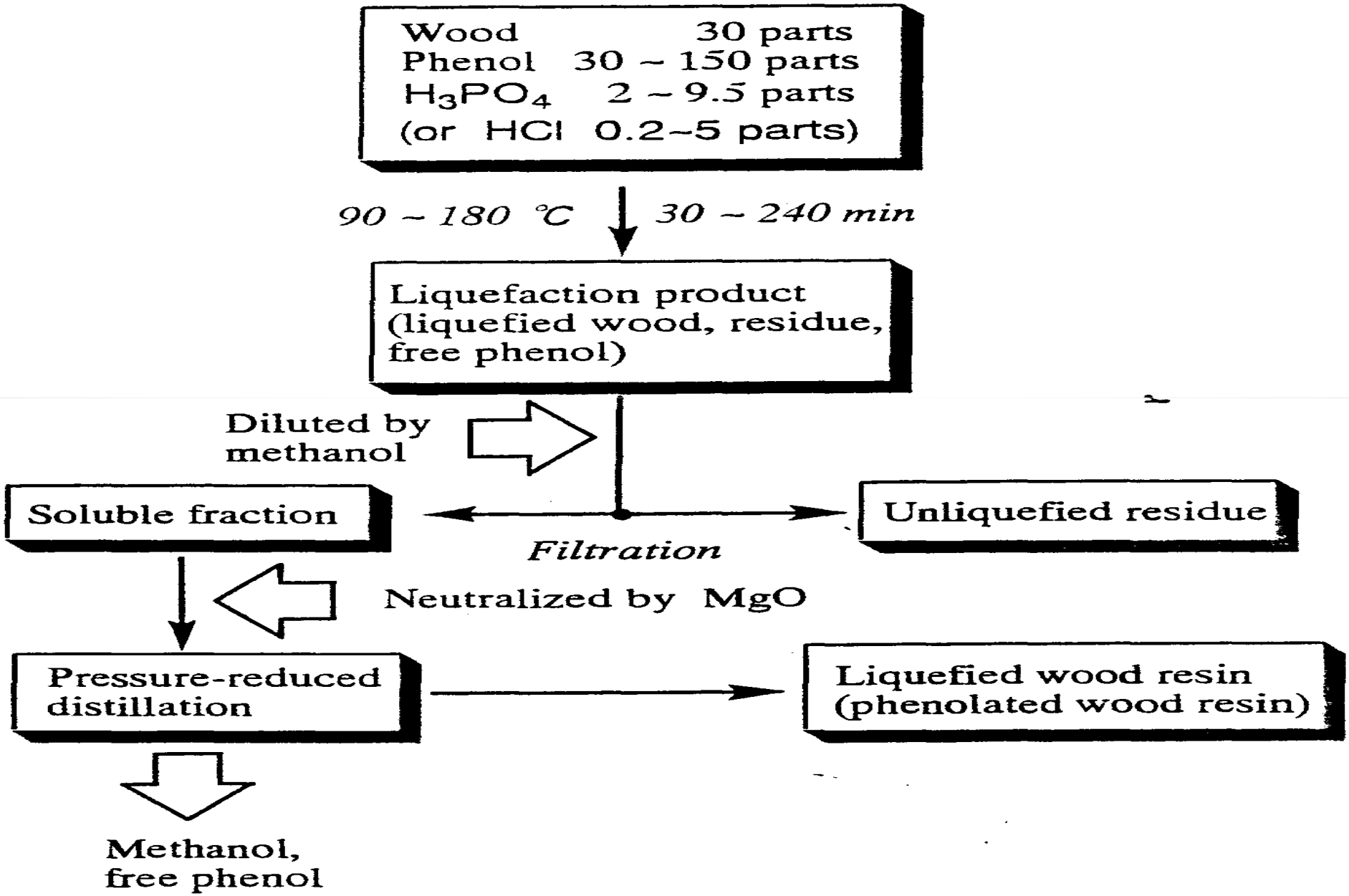
# Preparation chart of liquefied wood resins

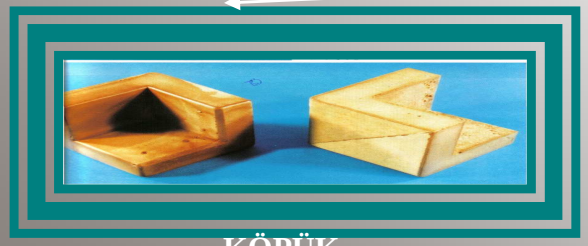


# ORMAN ENDÜSTRİ MÜHENDİSLİĞİ ANABİLİM DALINDA ÜRETİLEN ÜRÜNLER

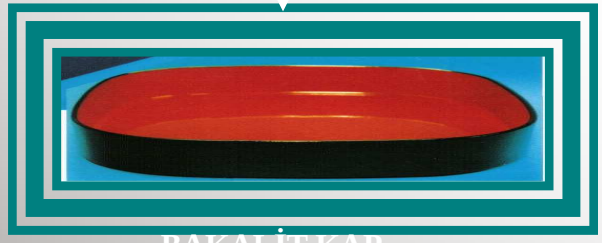
ODUN TALAŞI

SIVILAŞMA İŞLEMİ

SIVILAŞTIRILMIŞ ODUN TALAŞI



KÖPÜK



BAKALİT KAP

ÇOK TABAKALI KONTRPLAK

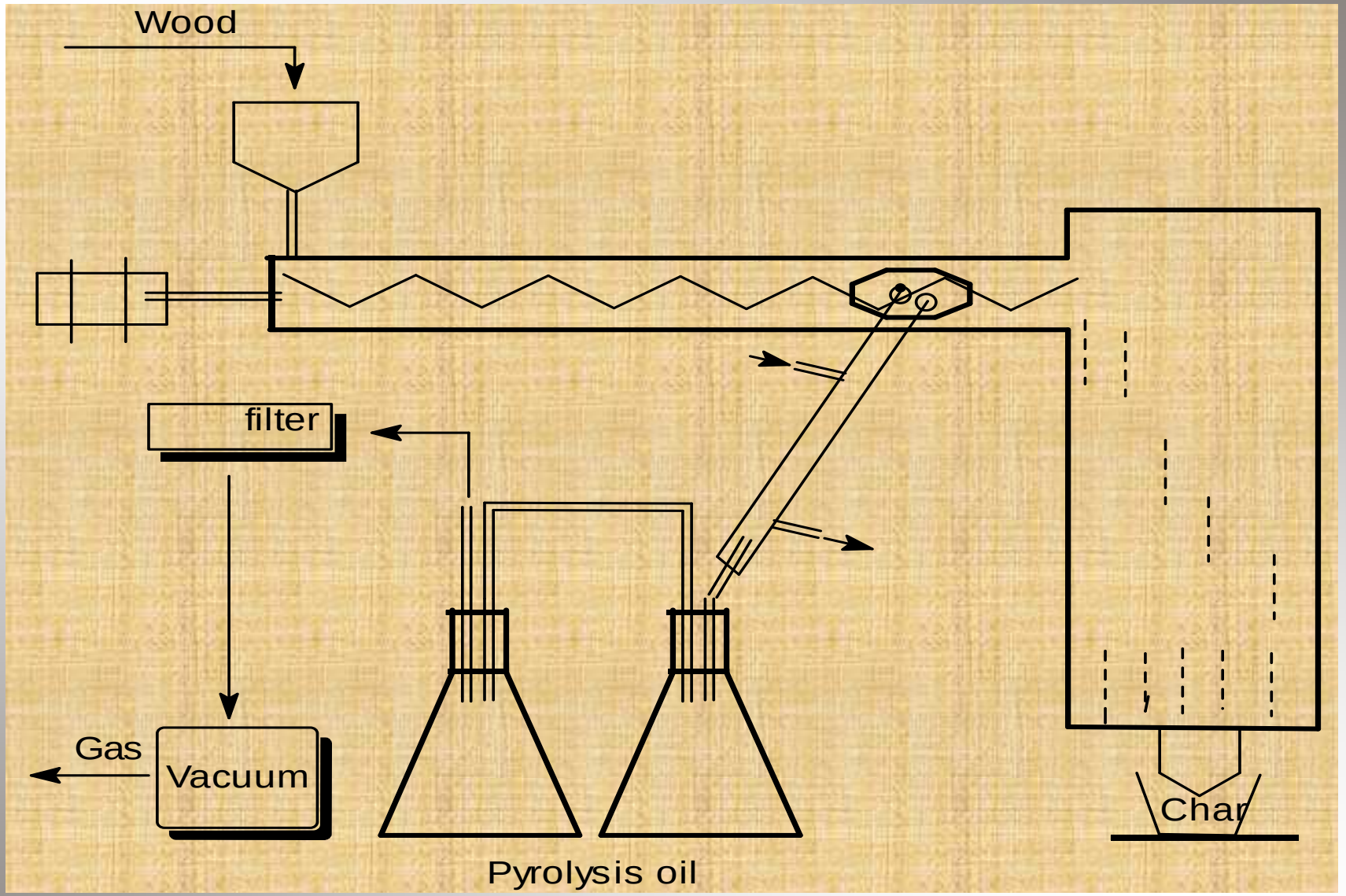
## Chemical composition of biomass (*Pinus sylvestris)* used.

| Composition | %* |
|---|---|
| Cellulose | 40.0 |
| Hemicellulose | 28.5 |
| Lignin | 27.7 |
| Extractives | 3.5 |
| Ash | 0.5 |

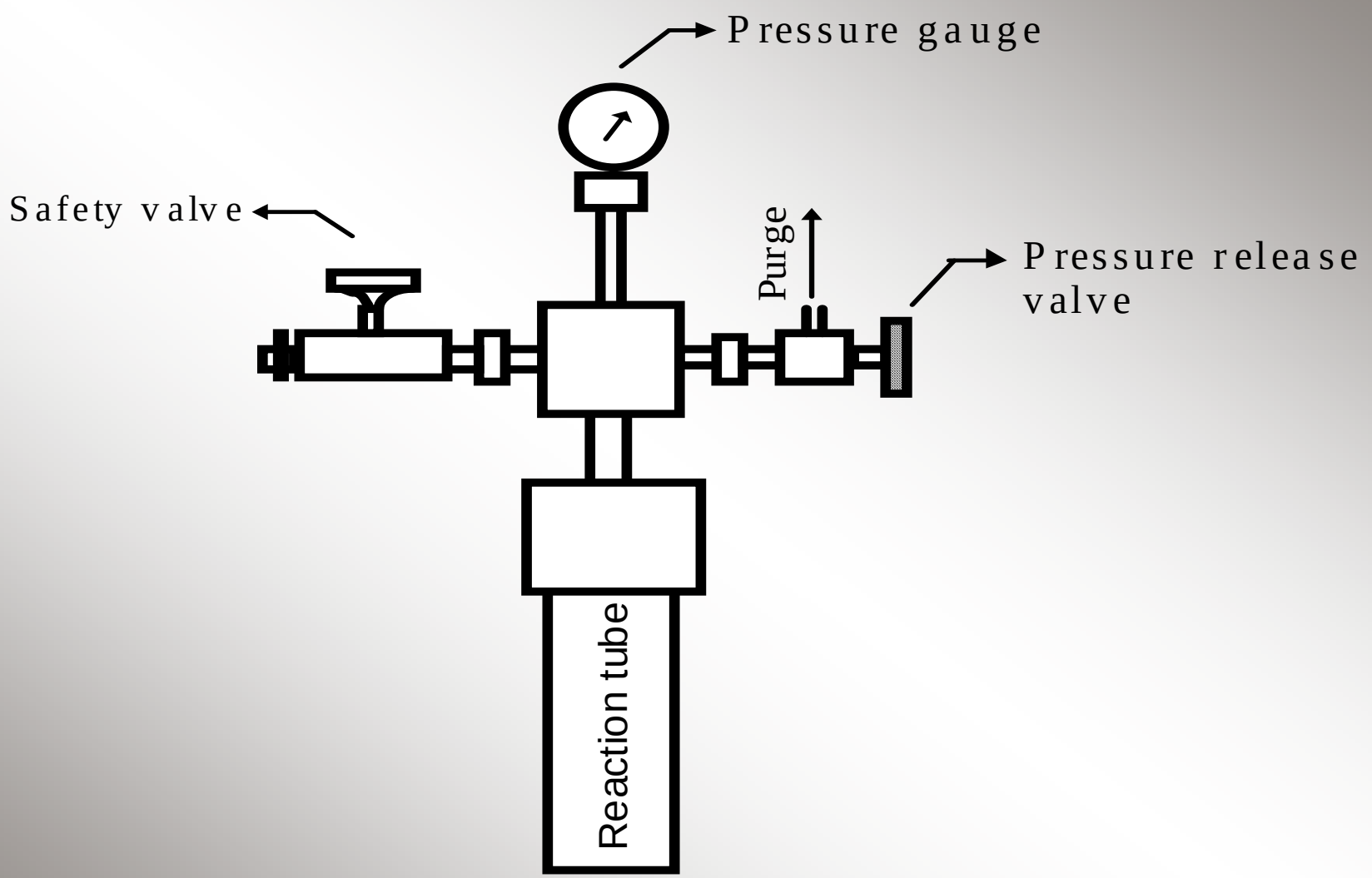
*Wt % oven dry and extractive free basis.

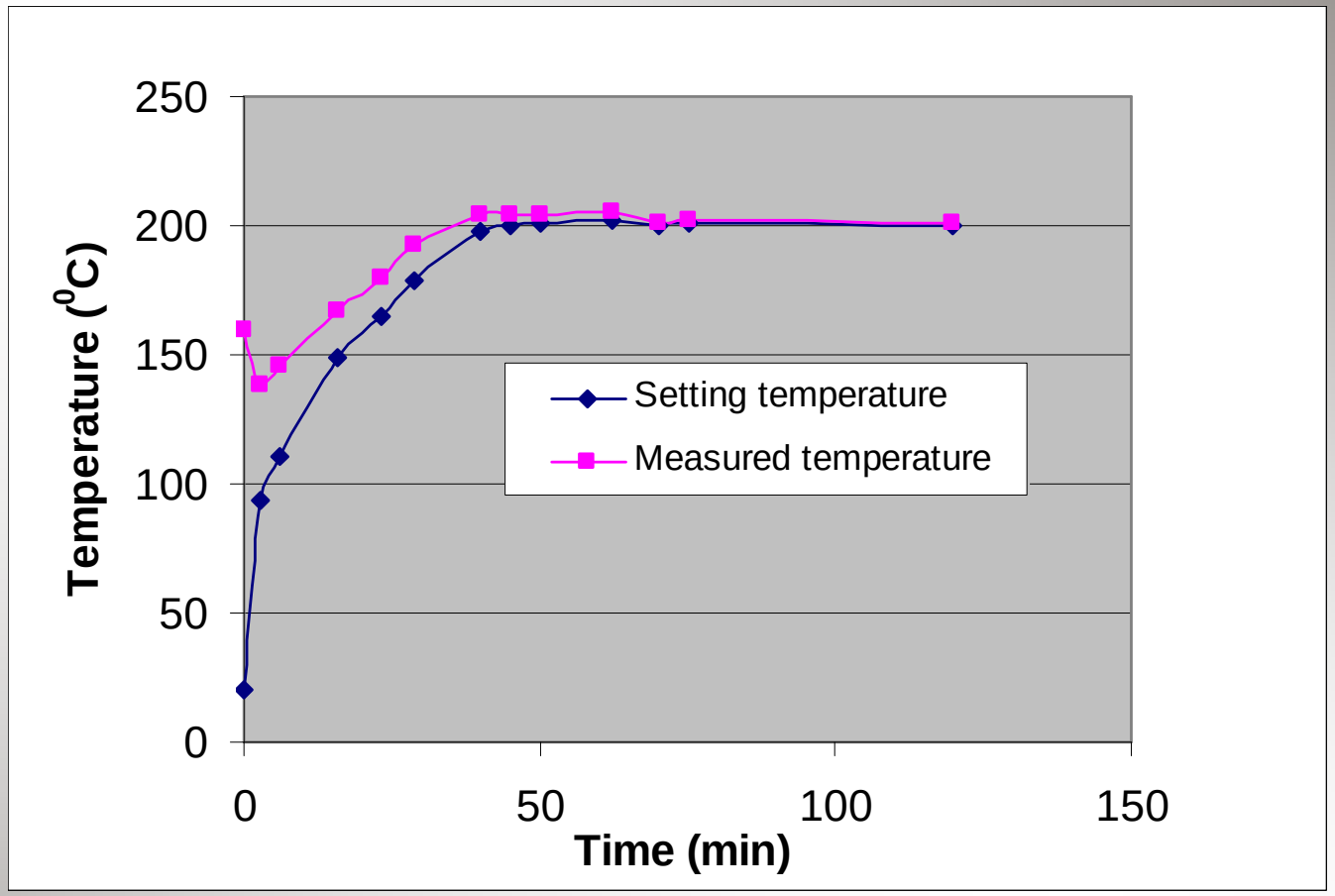
## Ultimate analysis of biomass used.

| Element (%, w) | *Pinus sylvestris* |
|---|---|
| C | 49.70 |
| O | 43.50 |
| H | 6.30 |
| S | 0.02 |
| N | 0.10 |
| Cl | 0.01 |
| Ash | 0.50 |
| Water | 7.10 |
| HHV [MJ/kg] | 19.24 |

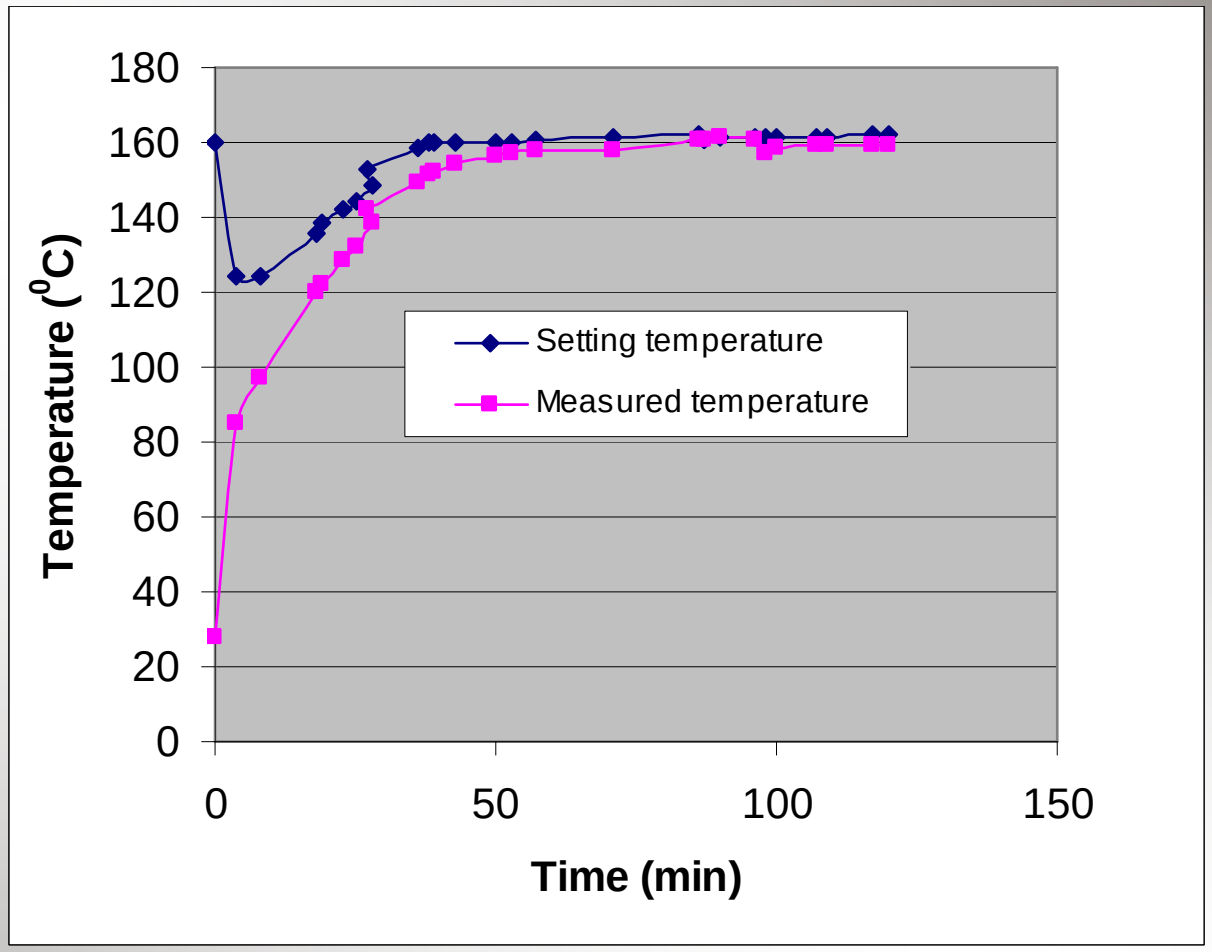



**Extruder type pyrolyzer.**

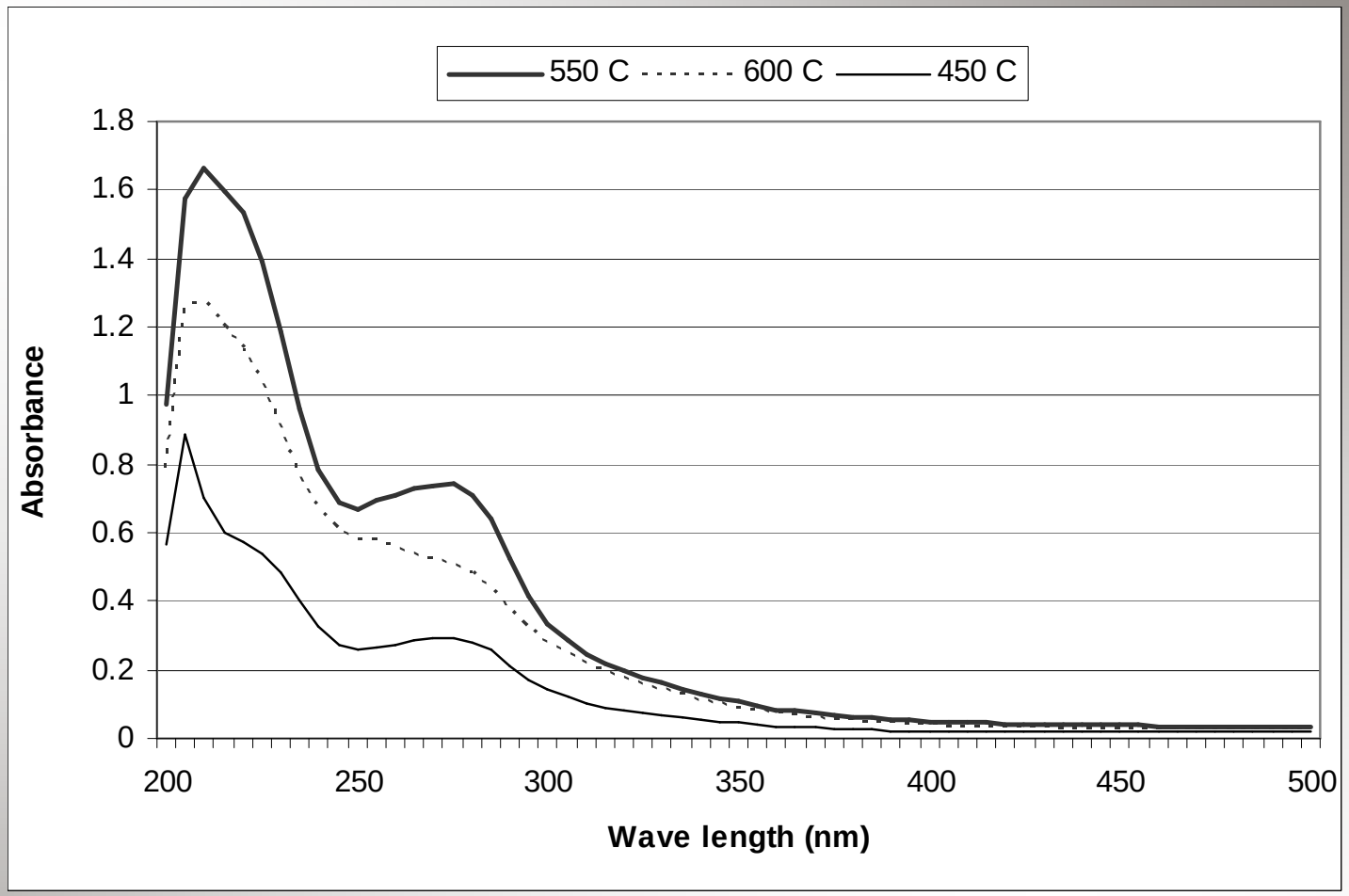

Pressure gauge
Safety valve
Purge
Pressure release valve
Reaction tube




**Profiles for setting and measured temperatures (Sample No: L7)**




**Profiles for setting and measured temperatures (Sample No: L2)**




**UV –vis absorbance curves for the pyrolytic oils studied.**

## Intensity determined at 270 nm as a function of pyrolysis temperature.

| Pyrolysis temperature ( ºC) | Intensity at 270 nm |
|---|---|
| 450 | 0.291 |
| 550 | 0.735 |
| 600 | 0.523 |

# The results of wood liquefaction with various types of pyrolytic oils.

| Sample No | Temp. (°C ) | Time (min) | Wood/Phenol/Pyrolytic-oil/Catalyst[1] | Residue (%)[2] | Liquefied fraction (%)[3] |
|---|---|---|---|---|---|
| | | | 450 °C Pyrolytic oil | | |
| L0 | 160 | 120 | 1/3/0/1 | 20 | 80.0 |
| L4 | 160 | 120 | 1/3/0/6 | 6.7 | 93.3 |
| L3 | 160 | 120 | 1/3/3.5/0 | 79.0 | 21.0 |
| L2 | 160 | 120 | 1/3/3.5/1 | 5.0 | 95.0 |
| L1 | 185 | 150 | 1/0/3/3 | 155 | Recondensation |
| L6 | 185 | 150 | 1/0/14/0 | 62.0 | 38.0 |
| L7 | 200 | 150 | 1/0/14/0 | 45.6 | 54.4 |
| L14 | 220 | 150 | 1/0/7/0 | 35.0 | 65.0 |
| L5 | 230 | 150 | 1/0/7/0 | 18.0 | 82.0 |
| L9 | 250 (450 °C light fraction) | 150 | 1/0/7/0 | 53 | Some recondensation |
| | | | 550 °C Pyrolitic oil | | |
| L10 | 220 (550 °C Heavy fraction) | 150 | 1/0/7/0 | 30.0 | 70.0 |
| L11 | 250 (550 °C Heavy fraction) | 150 | 1/0/7/0 | 2.5 | 97.5 |
| L12 | 250 (550 °C light) | 150 | 1/0/7/0 | 56.4 | 43.6 |
| L13 | 220 (550 °C Heavy oil and charcoal) | 150 | 1/0/7/0 (0.5 charcoal)[4] | 53.2 | 46.8 |

1Acid (90% $H_2SO_4$) concentration is based on the total amount of chemicals used (phenol and py-oil) in %.
2Acetone-insoluble fraction.
3Acetone-soluble fraction.
4Charcoal obtained after 2 stage partial oxidation gasification
Note: pH of pyrolytic oil: about 2.8. pH of the liquefied wood with py-oil is between 5 and 6.

## Chemical composition of the heavy fraction of pyrolytic oil obtained at a temperature of 550 ºC.

| No | Compounds[a] | RT[b] | %.[c] | Mol. Form. |
|---|---|---|---|---|
| 1 | Benzofuran | 9,57 | 1,94 | C8H6O |
| 2 | 2.5-dietoxytetrahydrofuran | 9,75 | 7,20 | C18H16O3 |
| 3 | 1pentanone,1-(4methylphenyl) | 10,1 | 0,61 | C12H16O |
| 4 | cis-beta-methylstyrene | 10,4 | 0,44 | C9H10 |
| 5 | Indan | 10,64 | 1,10 | C9H10 |
| 6 | 2-cyclopenten-1-one,2,3-dmethyl | 10,72 | 0,59 | C7H10O |
| 7 | p-Ethyltoluene | 10,97 | 2,39 | C9H8 |
| 8 | p-Diethylbenzene | 11,17 | 1,36 | C10H14 |
| 9 | 2-propenal,3-phenyl | 12,76 | 3,25 | C9H8O |
| 10 | Benzofuran,2-methyl | 12,87 | 3,02 | C9H8O |
| 11 | Octanoic acid, ME | 13,16 | 1,38 | C9H18O2 |
| 12 | Unidendified | 13,43 | 0,83 | - |
| 13 | Unidendified | 13,74 | 1,15 | - |
| 14 | Unidendified | 14,02 | 1,42 | - |
| 15 | Cyclopropane,Nonyl | 14,99 | 1,17 | C12H24 |
| 16 | 1H-indene,1-ethylidene | 15,28 | 5,04 | C11H10 |
| 17 | Unidendified | 15,52 | 0,87 | - |
| 18 | 1H-indazole,5,6,dimethyl | 15,61 | 1,18 | C9H10ON2 |
| 19 | 1H-indazole,5,7,dimethyl | 15,73 | 1,67 | C9H10ON2 |
| 20 | Benzofuran,4,7-dimethyl | 16,05 | 3,53 | C10H10O |
| 21 | Cyclopropane,1-methyl-2octyl | 17,81 | 1,50 | - |
| 22 | Nonanoic acid,methyl ester | 18,01 | 1,31 | C11H22O2 |
| 23 | 1H-indene,1-ethylidene | 18,42 | 3,08 | - |
| 24 | 2,5,6-trimethylbenzimidazole | 19,14 | 0,69 | C10H21N2 |
| 25 | beta damascone | 19,79 | 0,41 | C13H20O |

| | | | | |
|---|---|---|---|---|
| 26 | p-hydroxybenzalacetone | 20,12 | 0,34 | C10H10O2 |
| 27 | 1H-indazole,1,1,3,trimethyl | 20,41 | 0,86 | C13H26 |
| 28 | 1-tridecan | 20,55 | 1,67 | C13H26 |
| 29 | Biphenyl | 20,68 | 0,84 | C12H10 |
| 30 | Unidentified | 21,01 | 1,33 | - |
| 31 | Naphtalene,1,3,dimethyl | 21,71 | 1,75 | C12H12 |
| 32 | Naphtalene,1,5,dimethyl | 21,83 | 1,37 | C12H12 |
| 33 | Acenaphthylene | 22,63 | 3,33 | C12H8 |
| 34 | (3Z)-3-Hexadecene | 25,54 | 1,02 | C16H32 |
| 35 | Naphtalene,1-methyl-7(1-dimethylethyl) | 25,68 | 3,02 | C14H16 |
| 36 | Unidentified | 26,18 | 0,62 | - |
| 37 | Unidentified | 26,71 | 0,84 | - |
| 38 | 9H-Xanthene | 27,08 | 0,96 | C13H10O |
| 39 | Cyclotetracosane | 27,84 | 1,01 | C24H48 |
| 40 | Unidentified | 28,01 | 0,57 | - |
| 41 | Acenaphthylene,5-acetyl | 29,59 | 1,89 | C15H16 |
| 42 | 3-eicosene-(E) | 30,04 | 0,08 | C20H40 |
| 43 | 5-eicosene-(E) | 32,12 | 0,08 | - |
| 44 | pentadecanoicacid14-methyl ester | 32,85 | 1,58 | C17H34O2 |
| 45 | 6H-cyclopenta(def)phenanthrene | 33,34 | 1,35 | C15H10 |
| 46 | Phenanthrene,2,methyl | 33,47 | 0,75 | C15H12 |
| 47 | hexadecanoic acid ethyl ester | 34,2 | 1,69 | C18H36O2 |
| 48 | Unidentified | 35,01 | 1,76 | - |
| 49 | heptadecanoicacid ethyl ester | 35,52 | 1,06 | C19H38O2 |
| 50 | Phenanthrene,3,6-dimethyl | 35,68 | 0,90 | C16H14 |

| | | | | |
|---|---|---|---|---|
| 51 | Pyrene | 36,25 | 3,30 | C16H10 |
| 52 | Methyl 6-octadecenoate | 37,44 | 0,45 | C18H34O2 |
| 53 | Phenanthrene,2,3,5-trimethyl | 37,71 | 0,89 | - |
| 54 | 1-tricosan | 37,87 | 1,45 | C23H46 |
| 55 | Unidentified | 38,17 | 0,66 | - |
| 56 | Unidentified | 38,85 | 4,00 | - |
| 57 | 1-Phenanthrenecarboxylic acid,[d] | 41,32 | 1,41 | C21H30O2 |
| 58 | 1-Henicosyl formate | 42,26 | 1,13 | C22H44O2 |
| 59 | Benzofluoranthene | 43,47 | 0,61 | C18H10 |
| 60 | Benzanthrene | 45,41 | 0,35 | C1812 |
| 61 | Behenic acid, ME | 46,96 | 0,45 | C23H46O2 |
| 62 | 1,2-benzenedicarboxylyc acid mono(2-ethylhexyl)E | 47,15 | 0,32 | C16H22O4 |
| 63 | 7-oxodehydroabietic acid ME | 49,72 | 2,21 | C21H28O3 |
| 64 | Lignoceric acid methyl ester | 58,22 | 0,34 | C35H50O2 |
| 65 | Octanoic acid,ethyl ester | 61,71 | 0,49 | C20H40O2 |
| 66 | 7-Oxocholesteryl acetate | 63,22 | 0,68 | C28H46O3 |
| 67 | 7,8-Benzofluoranthene | 64,07 | 0,67 | C20H12 |
| 68 | Litholic acid | 69,85 | 1,77 | C24H40O3 |
| 69 | 4,6-Cholestadien-3alfa-ol | 71,09 | 0,68 | C27H44O |
| 70 | Cholest-5-en-3-ol(3beta)-carbonochloridate | 72,1 | 0,71 | C28H45O2Cl |

**aCompounds listed in order of retention time. b Retention time (as minutes). c Composition (%). d1-Phenanthrenecarboxylic acid 6,8-dichloro-1,2,3,4,4a,9,10,10a-octahydro-1,4a- dimethyl-7-(1-methylethyl)-, methyl ester, [1R-(1alfa,4alfa,10alfa)]**

**Chemical composition of the liquefied wood obtained at 250 ºC for 150 min by using for the heavy fraction of pyrolytic oil obtained at a temperature of 550 ºC.**

| No. | Compounds[a] | RT[b] | % [c] | Mol. Form. |
|---|---|---|---|---|
| 1 | Unidentified | 10,26 | 3,6 | - |
| 2 | Cinnamaldehyde,(E) | 12,75 | 0,63 | C9H8O |
| 3 | Unidentified | 12,86 | 3 | C14H30 |
| 4 | Octanoic acid ME | 13,1 | 1,15 | C9H18O2 |
| 5 | 1H-indene,1-methylene | 15,03 | 3,62 | C10H8 |
| 6 | Benzofuran,4,7-dimethyl | 16,01 | 2,28 | C10H10O |
| 7 | Unidentified | 17,57 | 4,72 | - |
| 8 | Naphtelene,2-methyl | 18,38 | 2,12 | C11H10 |
| 9 | 1H-indene,1-methyl | 18,82 | 2,65 | C11H10 |
| 10 | Unidentified | 21,87 | 8,35 | |
| 11 | 1.4-benzenedicarboxylyc acid, DME | 23,65 | 2,84 | C10H10O4 |
| 12 | Naphtelene,1-methyl-7-(1-methylethyl) | 25,27 | 0,31 | C14H16 |
| 13 | Unidentified | 25,74 | 3,19 | - |
| 14 | Flourene | 25,9 | 0,96 | C13H10 |
| 15 | 1,1-biphenyl,4-(1-methylethyl) | 29,55 | 1,25 | C15H16 |
| 16 | Phenantrhrene | 30,44 | 2,26 | C14H10 |
| 17 | Hexadecanoic acid ME | 32,85 | 2,31 | C17H34O2 |
| 18 | Phenantrhrene,3,6-dimethyl | 35,76 | 0,62 | C16H14 |
| 19 | 7-Isopropyl [d] | 36,5 | 1,28 | C18H22 |
| 20 | Octadecanoic acid ME | 36,71 | 1,73 | C18H38O2 |
| 21 | Flouranthene | 37,24 | 2,53 | C16H10 |
| 22 | Phenantrhrene,2,3,5-trimethyl | 37,66 | 0,75 | C17H16 |
| 23 | Unidentified | 38,14 | 1,79 | - |
| 24 | 2-isopropyl-10-methylephenanthrene | 38,77 | 3,44 | C18H18 |

aCompounds listed in order of retention time. b Retention time (as minutes). c Composition (%). d1-Phenanthrenecarboxylic acid 6,8-dichloro-1,2,3,4,4a,9,10,10a-octahydro-1,4a- dimethyl-7-(1-methylethyl)-, methyl ester, [1R-(1alfa,4alfa,10alfa)]

Table 7. High heating value of liquefied wood oil from pyrolytic oil and pyrolytic oil itself.

| Oils | HHV (kcal/kg) |
|---|---|
| 450 | 5523 |
| 550 | 7240 |
| 600 | 6299 |
| | |
| L 5 | 6374 |
| L 6 | 4327 |
| L 7 | 5989 |
| L 10 | 7240 |
| L 12 | 6827 |
| L 12 | 5394 |
| L 13 | 6915 |

**Appearance of pyrolytic oil (left), wood biomass (middle) and Liquefied biomass (right).**

L3; RESIDUE: 79%

L6; RESIDUE: 62%

L7; RESIDUE: 45%

L5; RESIDUE: 18%

**Appearance of residue obtained for various reaction conditions.**

- Conclusions

- Wood powder can easily be liquefied by using pyrolytic oil obtained from the same wood
- The most adequate py-oil is the one prepared at pyrolysis temperature of 550 C.
- Chemical composition of pyrolytic oil was changed after liquefaction process.


THANK YOU