Fractional catalytic pyrolysis of biomass to stable biooils and hydrocarbon fuels

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Objectives

- Develop low temperature catalytic process to produce stable pyrolysis oils
  - Develop suitable catalysts for the process
  - Pyrolyze the biopolymer components independently
  - Pyrolysis and catalysis occur simultaneously

Biomass Constituents

Lignin: 15-25%

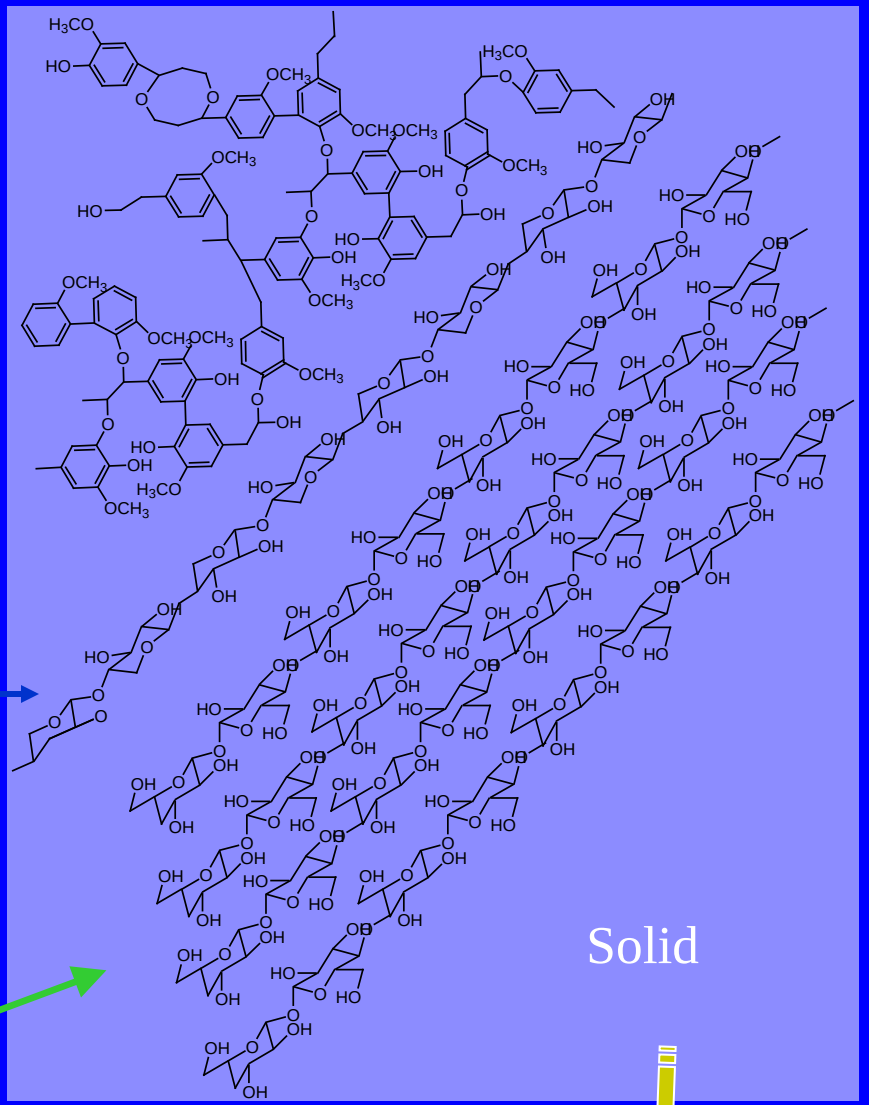
- **Complex aromatic structure**
- **Very high energy content**

Hemicellulose: 23-32%

- **Polymer of 5 & 6 carbon sugar**

Cellulose: 38-50%

- **Polymer of glucose, very good biochemical feedstock**

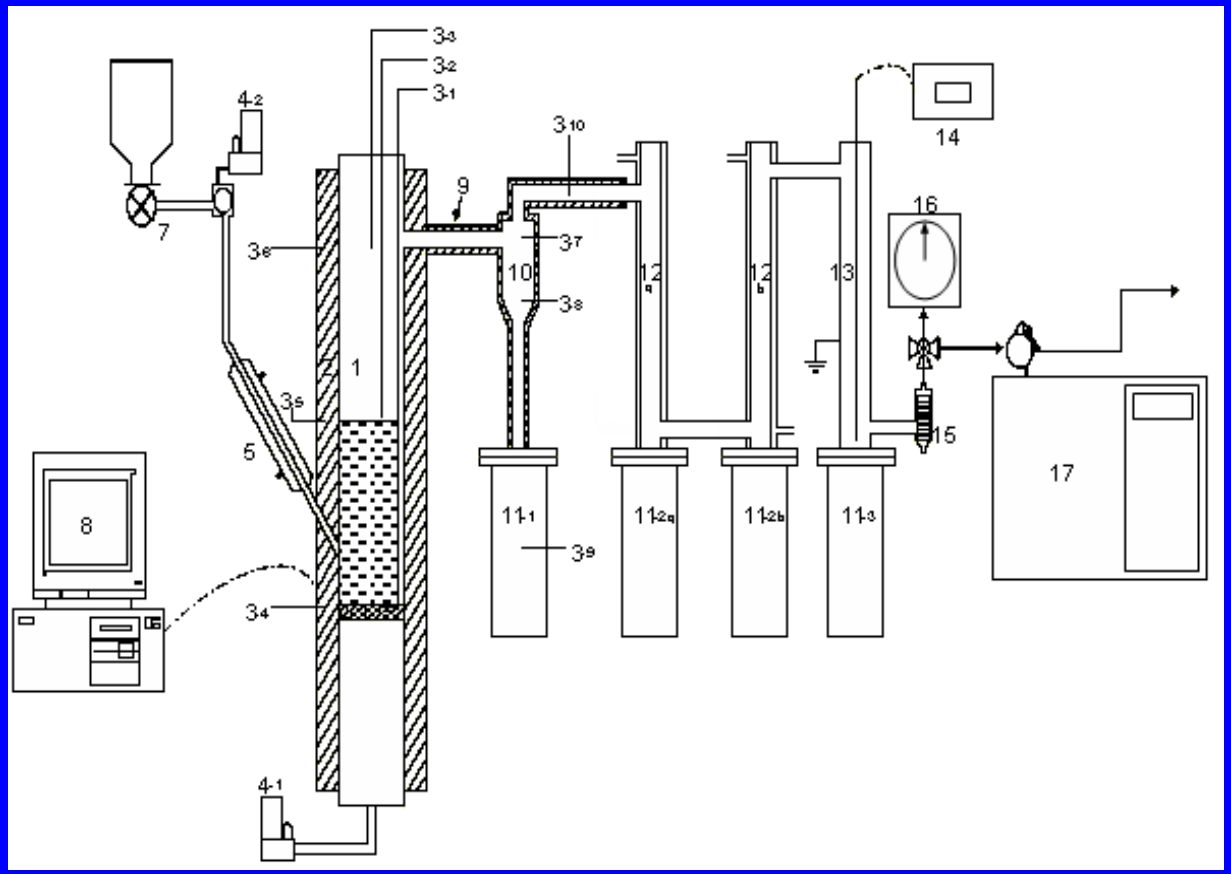


Gas or Liquid

Materials and Methods

- **Materials**
  - Hybrid poplar wood, corn stover- ground to pass 1-mm screen
  - Proprietary catalyst/silica sand
  - Fluidizing gas --Nitrogen
- 2-inch Bubbling fluidized bed reactor

Biomass Catalytic Pyrolysis Unit



1- Fluidized bed reactor,
3- Thermocouple,
4- Mass flow controller,
5- jacketed air-cooled feeder tube,
6- Hopper,
7- Screw feeder,
8- Computer,
9- Heating tape,
10-Hot gas filter,
11-Reservoir,
12-Condenser,
13-ESP,
14-AC power supply,
15-Filter,
16-Wet gas meter,
17-Gas chromatograph)

Materials and Method

- Method
- Pyrolysis temp = 450 C
- Vapor residence time = 1 s
- Electrostatic precipitator at 18-20 kV
- Run time – 2-3 hours
- Biomass feed rate 100 g/h.
- Catalyst = 150 g

Materials and Method

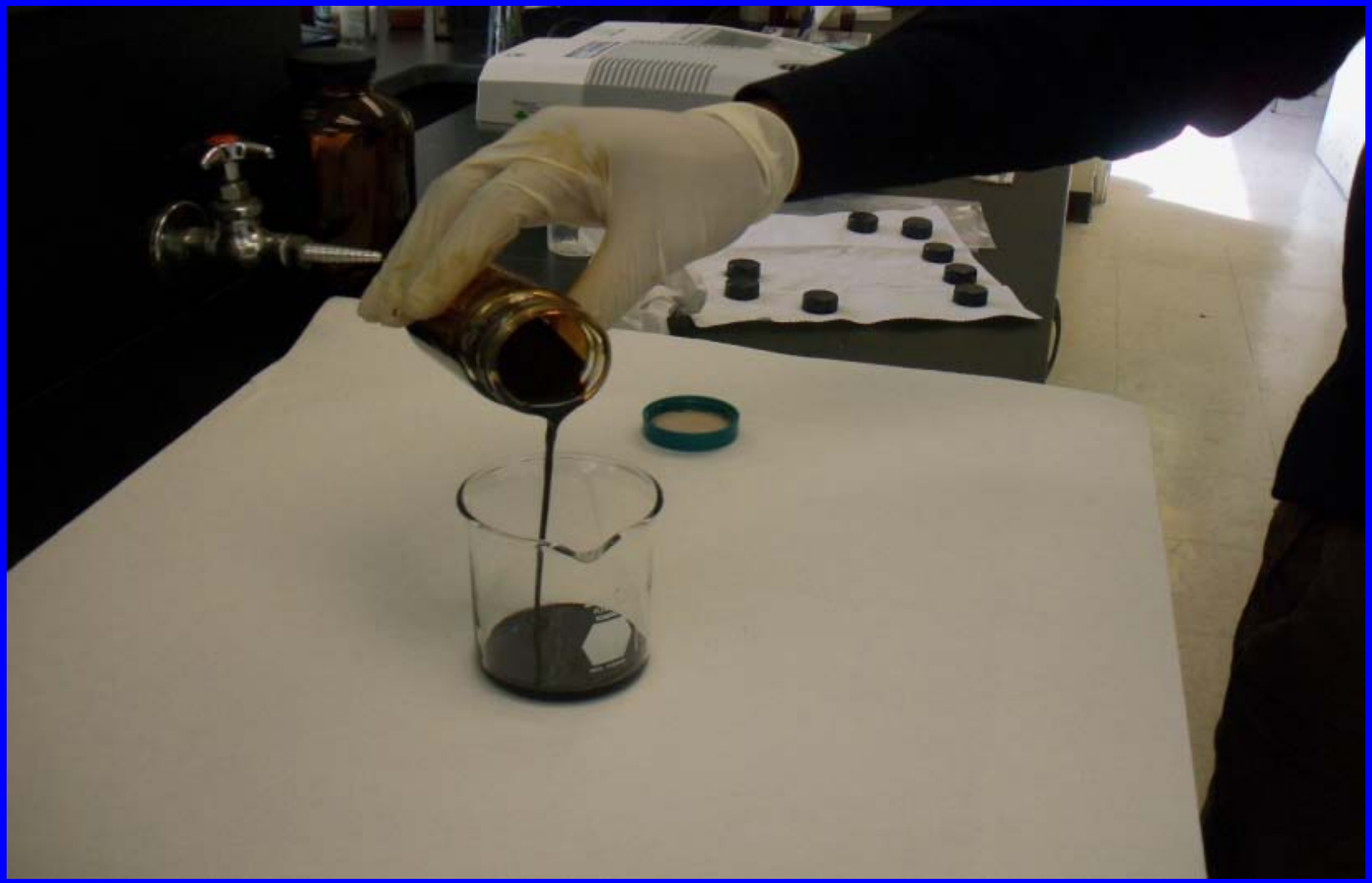
- Analysis
  - FTIR and ^{13}C NMR analysis of oils
  - High temperature simulated distillation
  - GC analysis of gases

Results and Discussion

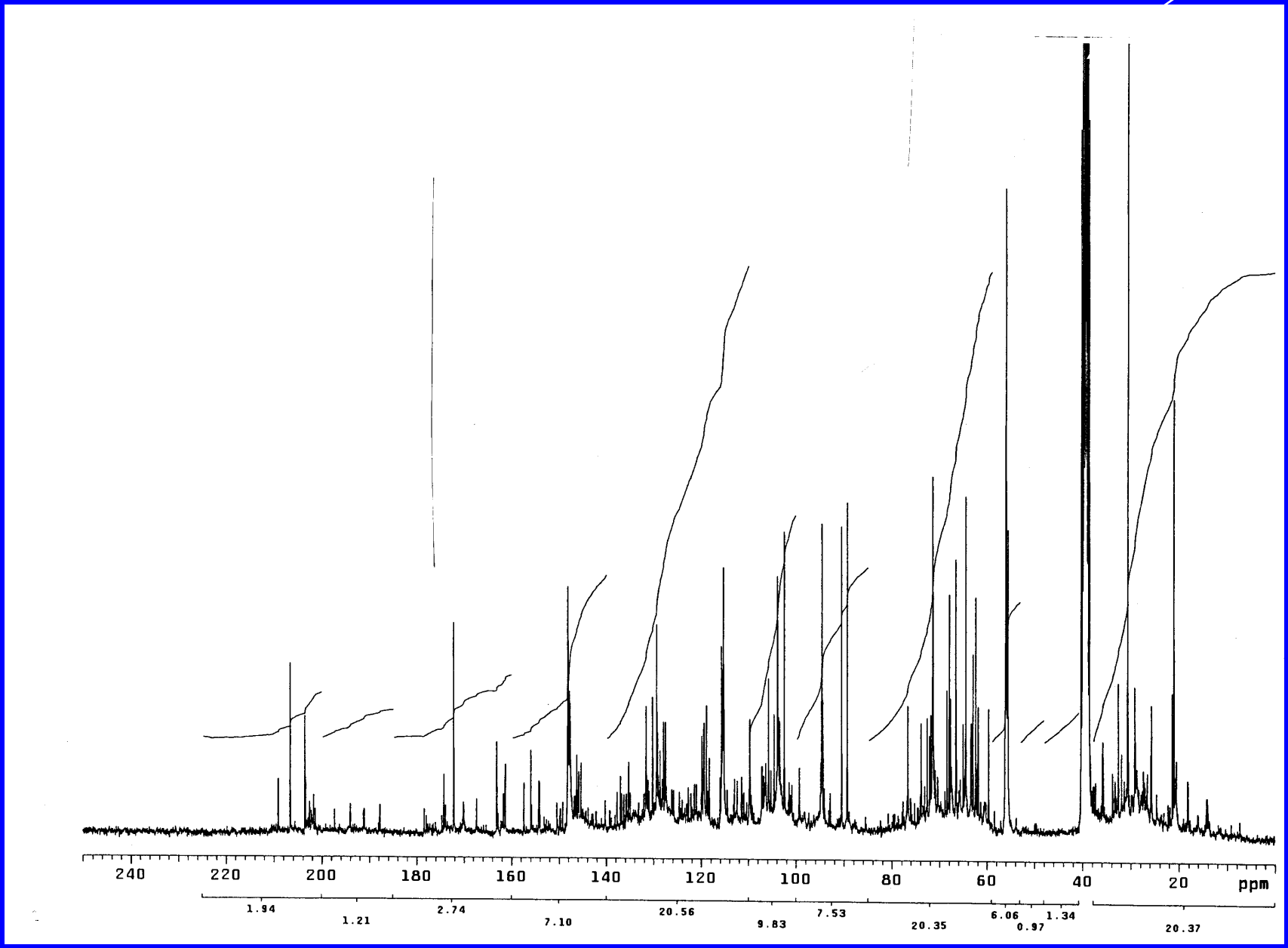
Product yields

Biomass	FCP oil (wt%)	Char (wt%)	Gas (wt%)	Oil pH
Hybrid poplar	33.3	12.2	55.0	3.4
Pinewood	43.3	35.1	21.5	3.3
Oakwood	41.8	33.8	24.6	4.4
Corn stover	40.1	24.8	35.5	4.2
Switchgrass	35.5	27.6	36.7	4.2

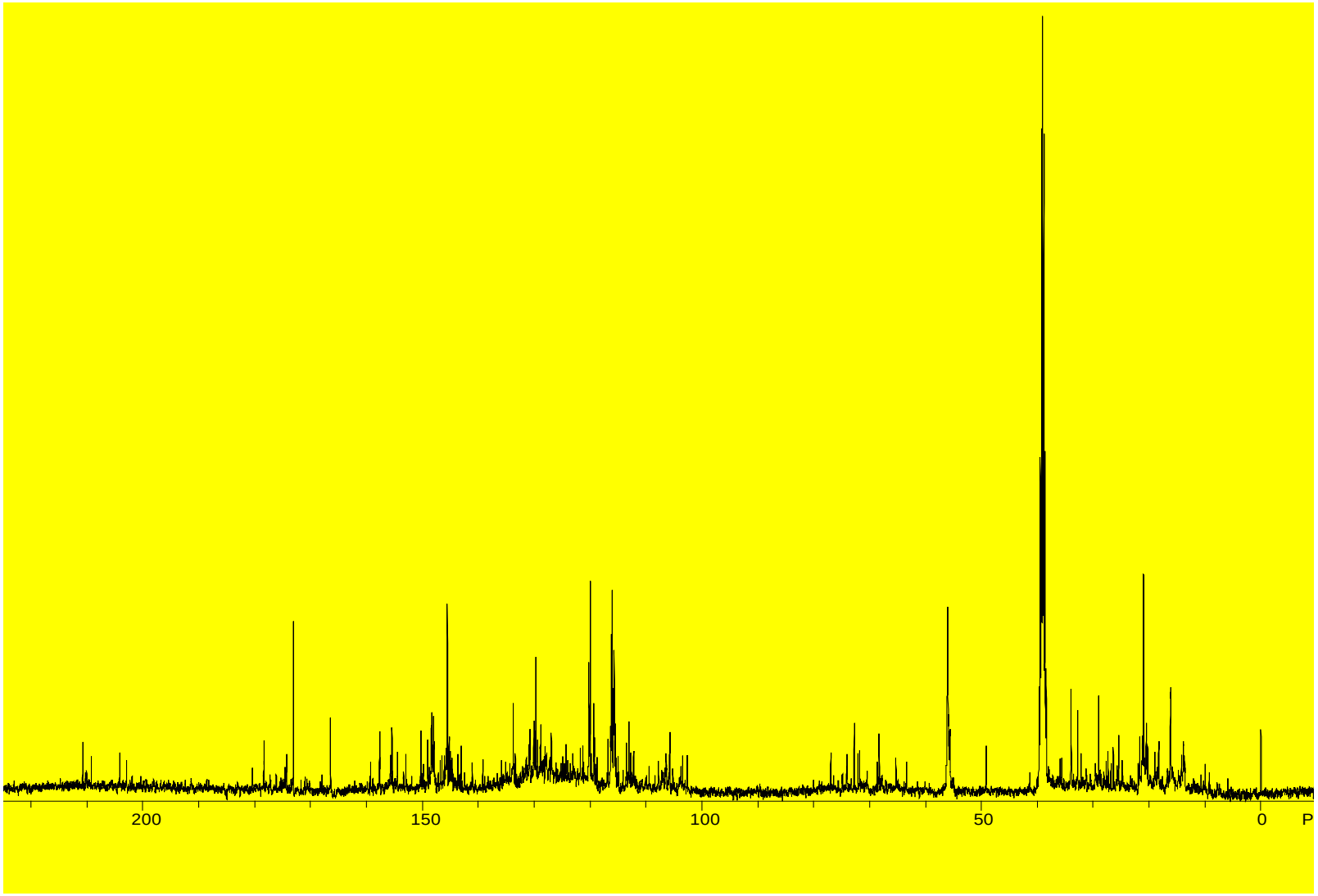
Hybrid poplar FCP oil



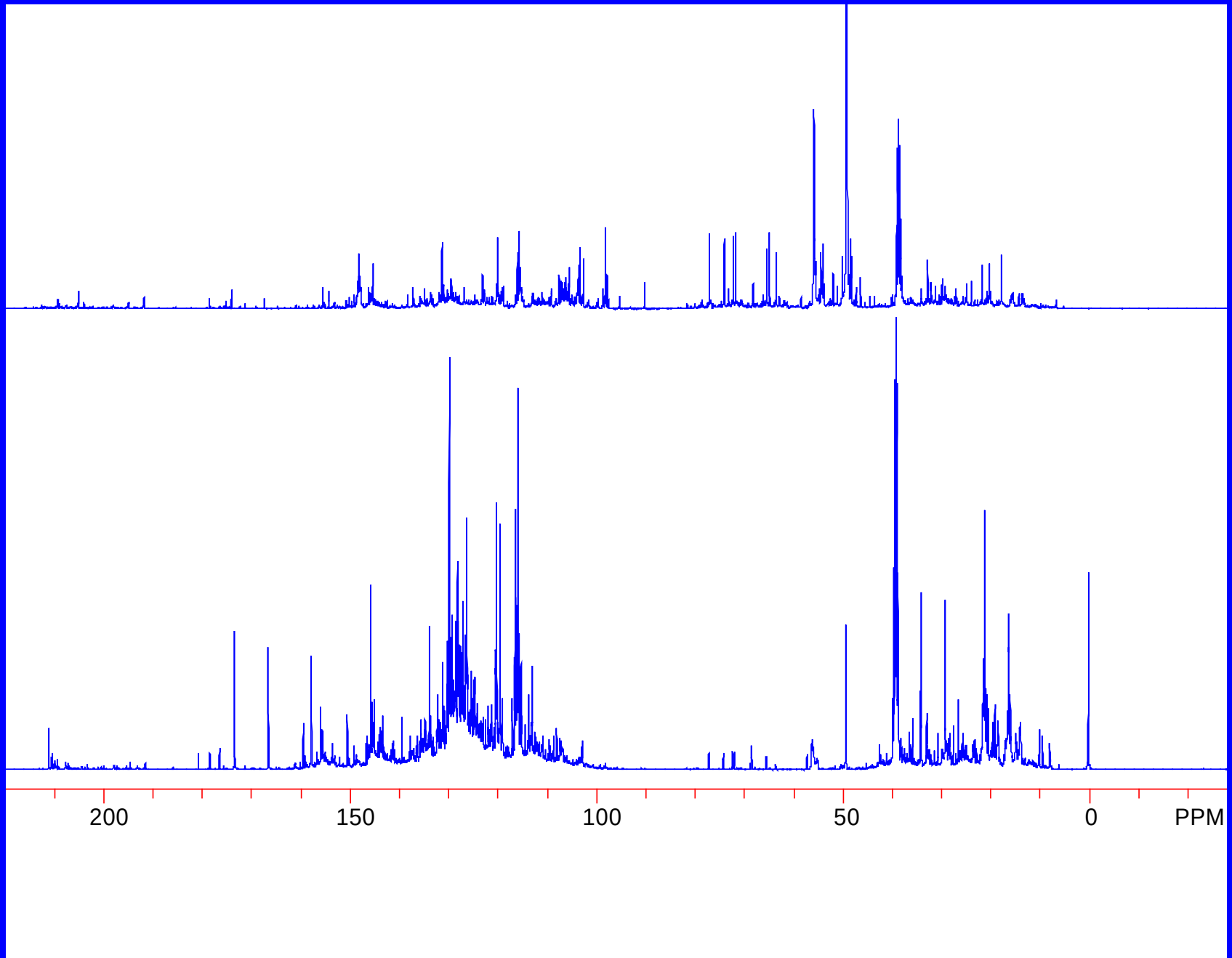
^{13}C NMR of non-catalytic pyrolysis oil



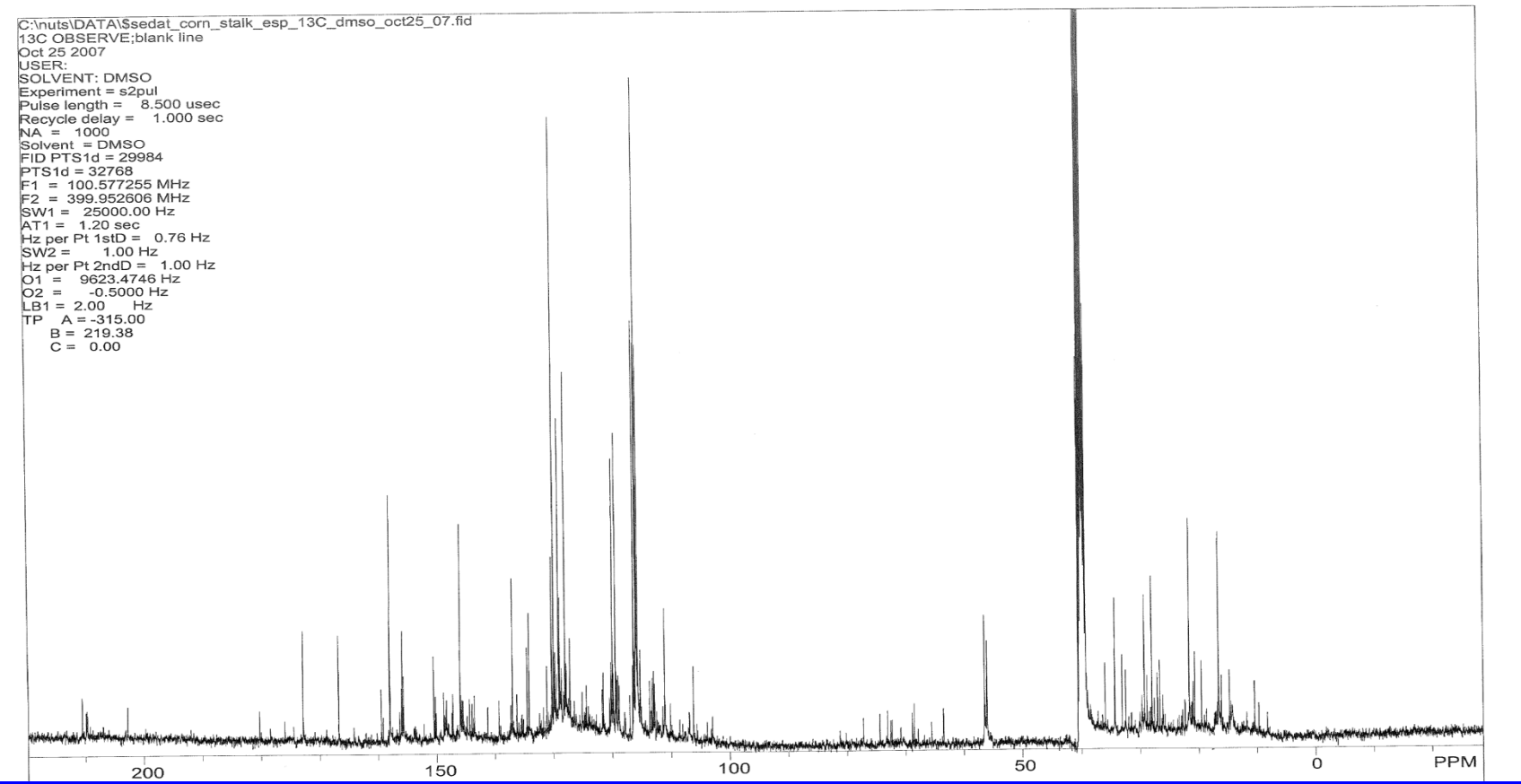
^{13}C-NMR SPECTRUM OF VPI4 WOOD PYROLYSIS OIL



^{13}CNMR SPECTRA OF STABLE WOOD BIOOILS



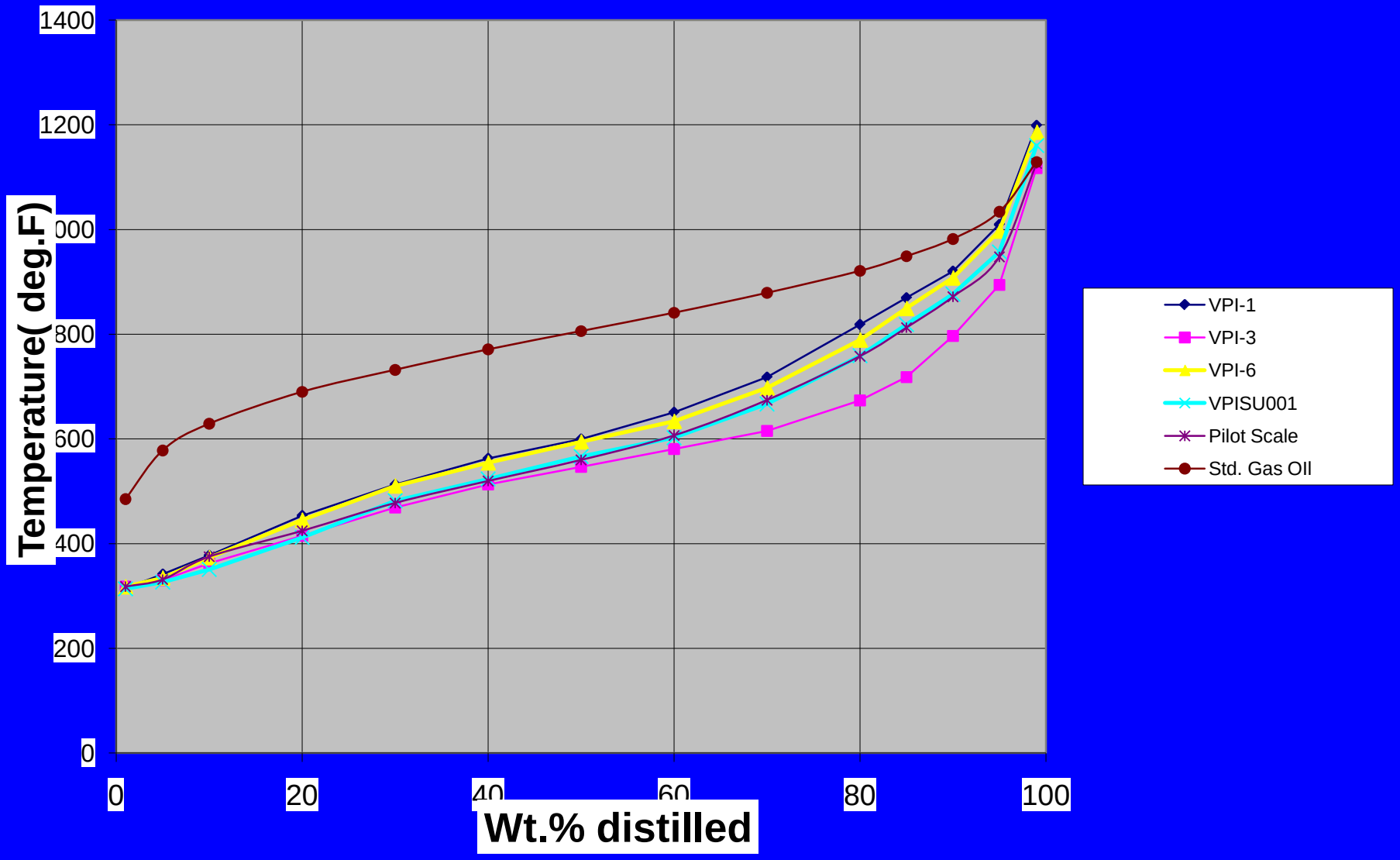
Corn stover catalytic pyrolysis oil



Storage stability of hybrid poplar FCP oils

	Fresh RP oil	Fresh FCP oil
Viscosity (cP) @40 ^{o}C	56.27±0.12	11.24
Karl Fischer Moisture (%)	23.74±1.87	8.59
pH	2.53±0.03	3.53±0.04
Density (g/cm^3)	1.216±0.001	1.116±0.001
TAN (mg KOH/g biooil)	90.05 ±1.89	41.02 ±0.82
Stored oil	**Stored oil after 180 days**	**Stored oil after 314 days**
Viscosity (cP) @ 40 ^{o}C	90.2	12.70
Karl Fischer Moisture (%)	n/a	8.66
pH	n/a	3.73
Density (g/cm^3)	n/a	1.117

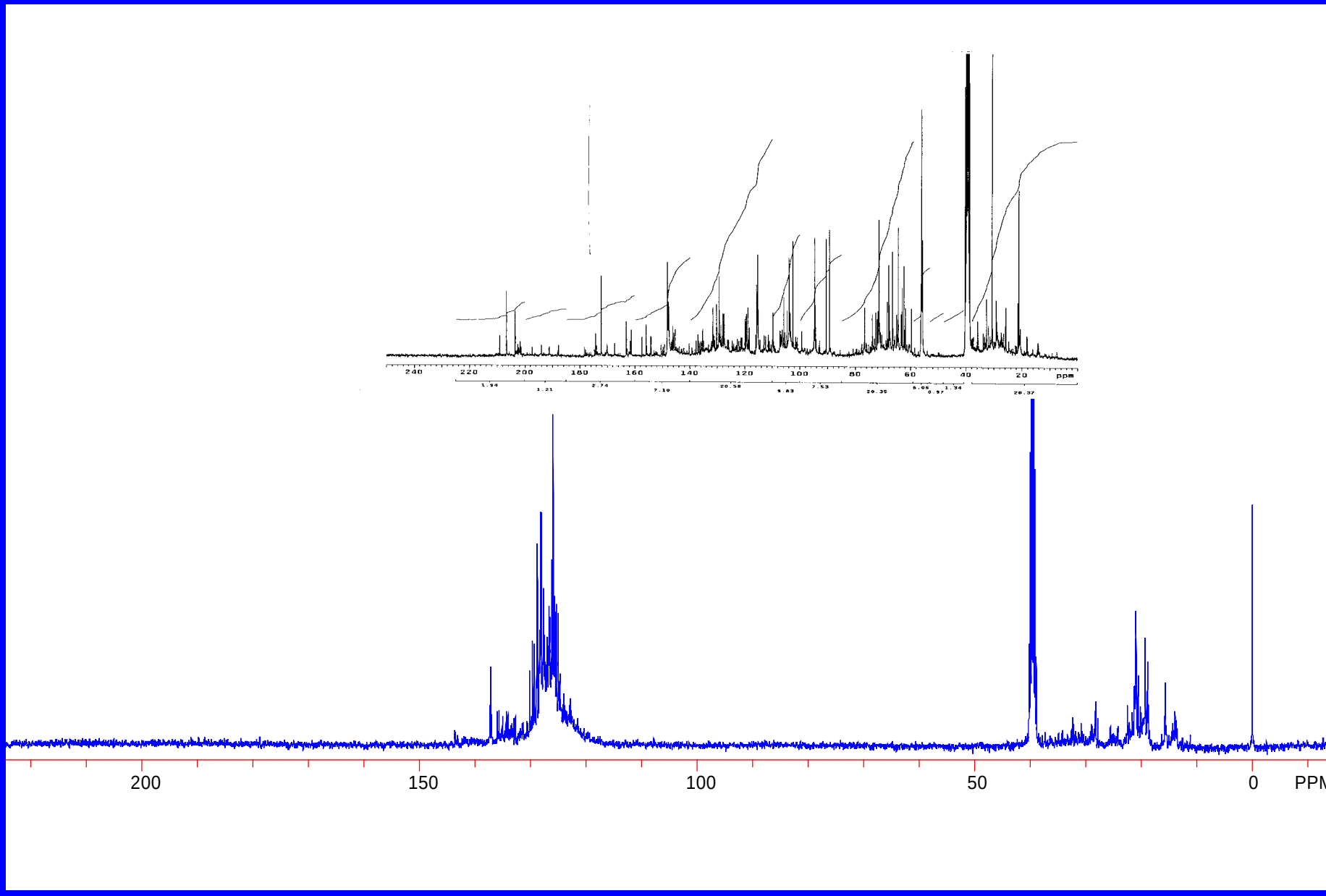
Standard gasoil and Biooils distillation curves



FCC Co-Cracking Data

	Standard 4350	VPI-4	VPI-4ST	VPISU001
H2 (%)	0.61	0.53	0.44	0.56
Total C2- (%)	2.98	2.99	2.92	2.94
LPG (%)	16.00	16.19	16.00	15.95
Gasoline (%)	43.97	44.01	44.44	44.35
LCO (%)	17.06	16.93	17.23	17.23
HCO (%)	12.94	13.07	12.77	12.77
Coke (%)	7.06	6.81	6.64	6.76
Conversion (%)	70.00	70.00	70.00	70.00
Cat/Oil	6.00	6.08	5.96	5.81

^{13}CNMR SPECTRUM OF FCC CRACKED BIOOIL/GASOIL BLEND



Advantages of new Technology

- No hydrogenation stabilization treatment
- Boiling point of “biosyncrude” similar to light petroleum crude but has no sulfur
- “Biosyncrude” could command the same price as “sweet crude” or possibly higher premium over standard crude because it has very low high boiling residuum
- Initial conversion step could produce saleable transportation fuels

What next?

- Develop integrated pilot processing facility to generate products to characterize and qualify

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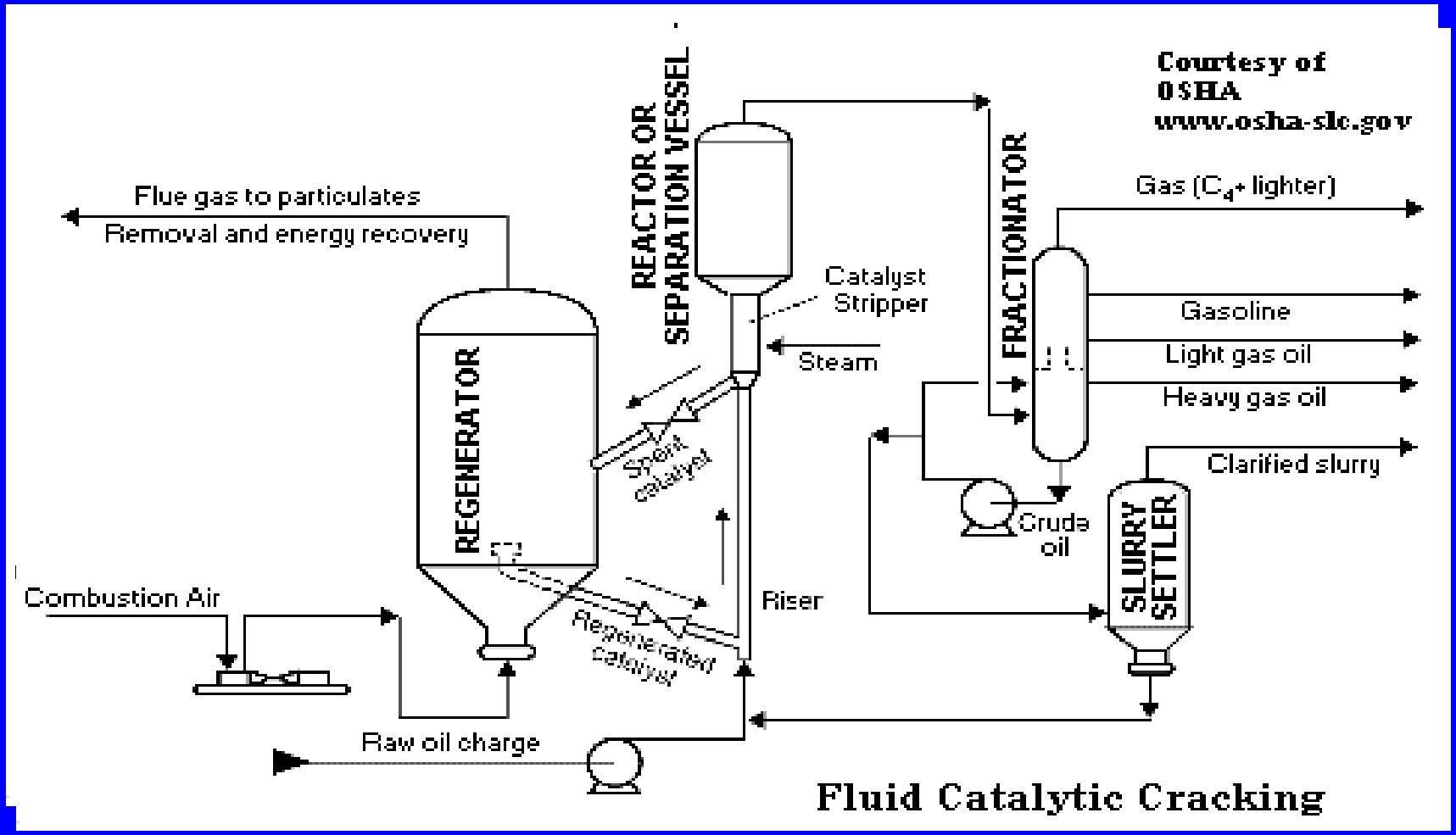
Pilot plant for biooil production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Crude oil
SLURRY
SETTLER
Combustion Air
Riser
Regenerated catalyst
Raw oil charge
Fluid Catalytic Cracking

Summary

- We have developed a process to produce stable FCC-crackable pyrolysis oils.
- The viscosity of the stable pyrolysis oil increased from 10.1 cSt to 11.4 cSt after ten months of storage at ambient laboratory conditions
- The stable pyrolysis oils were completely distillable without char formation (no residuum)
- 85/15 blend of Standard Gulf coast FCC feed and stable pyrolysis oils were crackable without any problem. The blend produced slightly less coke than the Standard Gulf coast FCC feed cracked under similar conditions

Summary

- How transformational is the technology?
- Pyrolysis oils could be co-processed in existing petroleum refineries
- Existing petroleum refineries could claim “green credits” by processing the biosyncrude.

Acknowledgement

- DOE for funding the pyrolysis oil stability studies.
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Thank you!!

- Questions?