Technical Information Exchange on Pyrolysis Oil:
Potential for a renewable heating oil substitution

Challenge # 3 – *Operational Issues*

What are the most significant barriers to overcome in each market segment?

Fernando Preto

CanmetENERGY
Leadership in ecoInnovation

Challenges – Operational Issues

The challenge is to identify the technical knowledge gaps that need to be closed order for industry to establish the infrastructure to address wide-spread utilization of pyrolysis oils:

- compatability (blending) with existing hydrocarbon fuels
- long term storage stability
- containment, handling and corrosivity
- fouling and plugging
- burner design and combustion performance

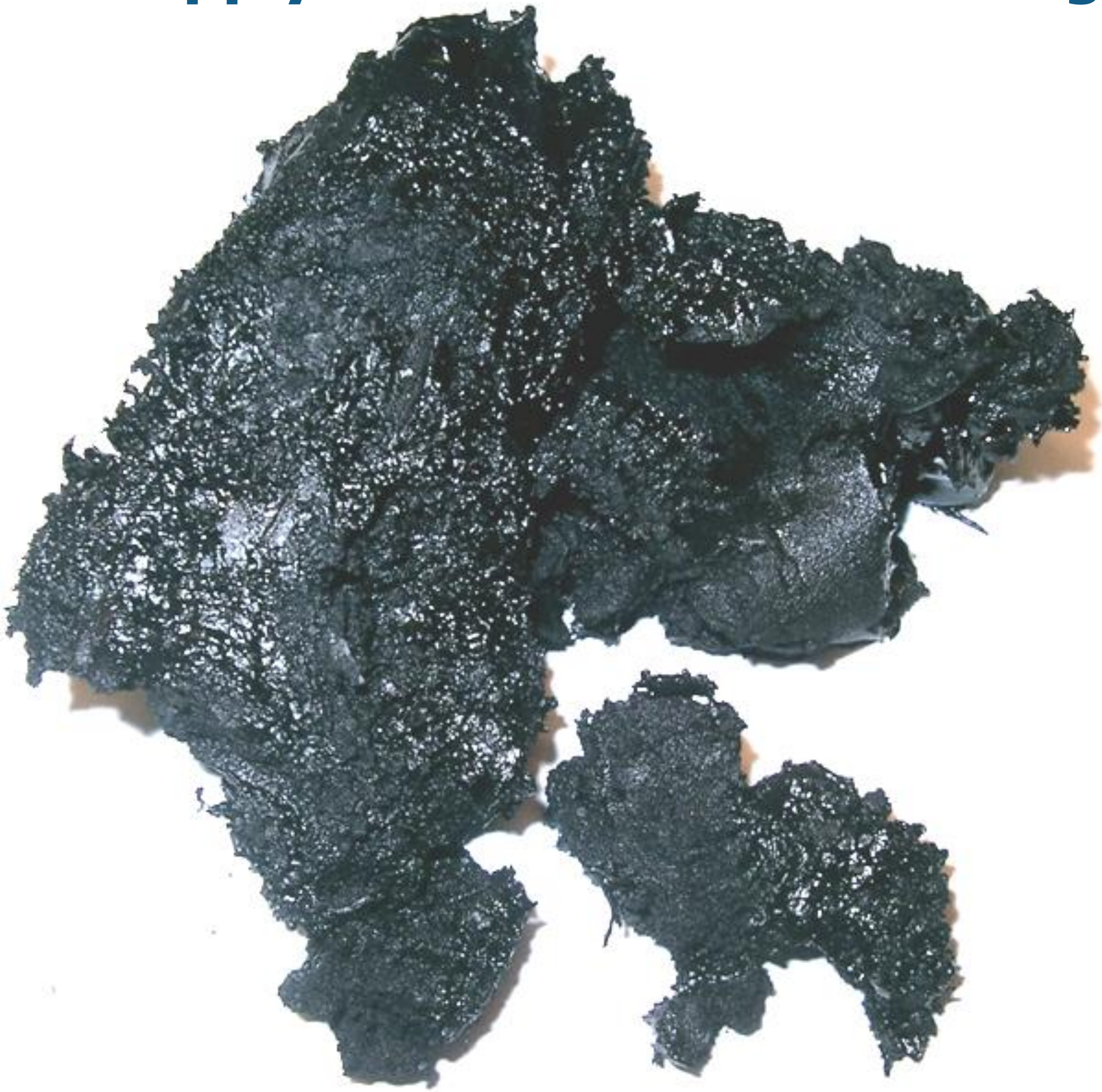
Aside from the knowledge gaps, infrastructure-related requirements and/or regulations must also be addressed:

- technical standards including WHMIS issues: hazard identification and product classification, labelling, material safety data sheets, and worker training and education.
- spillage and emissions monitoring/regulations
- government incentives for infrastructure development

Challenges – Stabilization / Upgrading / Blending

- Stability can be addressed by adapting the chemistry of the molecular fragments in the initial pyrolysis step e.g. vapour phase catalysis, removal of polymerization inducing "materials" e.g. ultra-filtration, upgrading of pyrolysis oil to a stable intermediate or hydrocarbon fuel. On the other hand, stabilization can also be addressed by blending with a solvent e.g. alcohol.
- **Is stabilization required for a heating fuel substitution application? Which approach best lends itself to this end-use? Upgrading? Blending? Fractionation?**

Coking in Supply Line Due to Overheating of Bio-oil



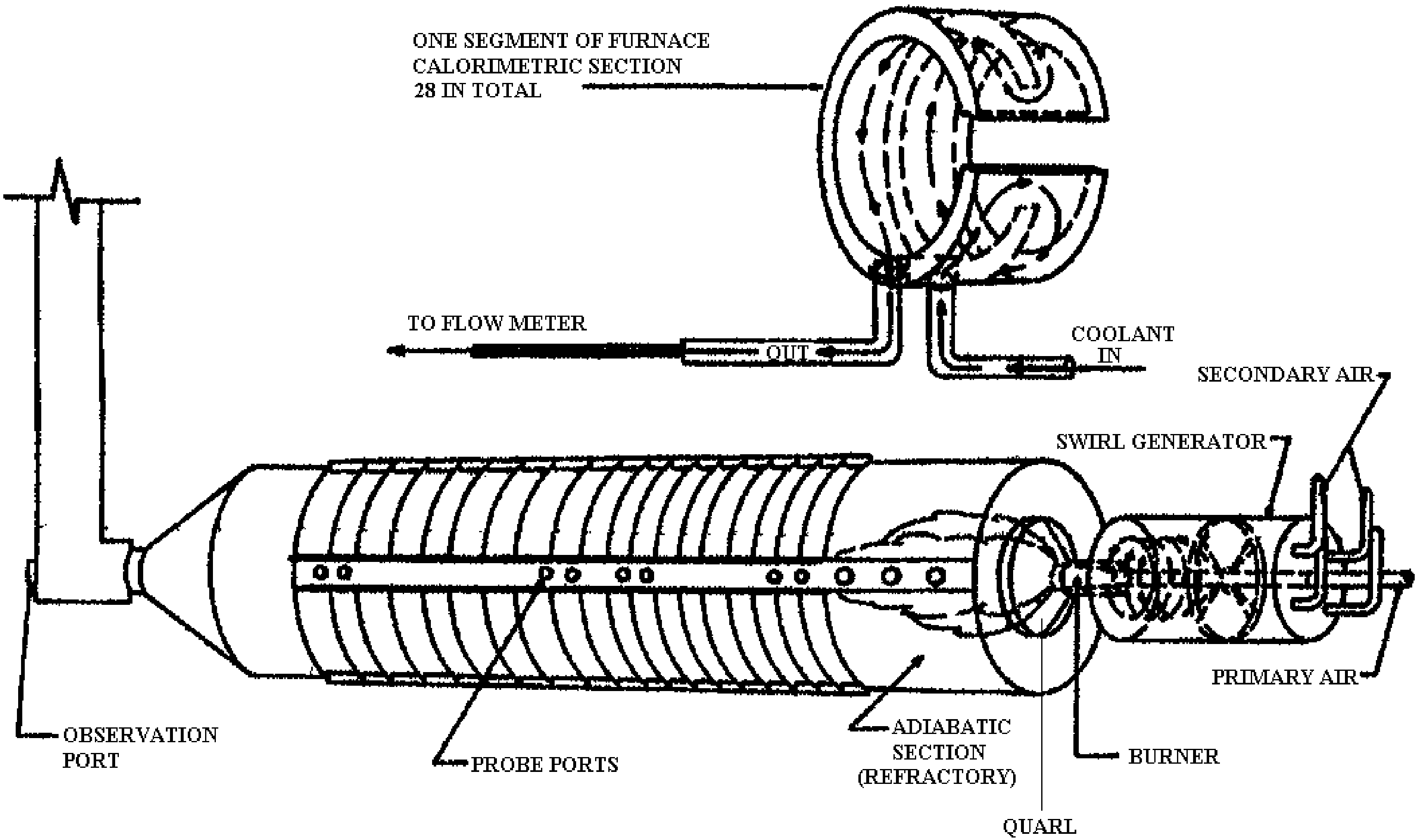
Challenges – Combustion

- Combustion of pyrolysis oils by co-firing has been successfully demonstrated at a number of laboratories and industrial sites. A number of labs have also demonstrated combustion of filtered, diluted (usually with alcohol) pyrolysis oils in burners, internal combustion and Stirling engines. There is limited experience in combustion of "untreated" undiluted pyrolysis oil. In the latter area, ignition, control and especially "cold start performance" have been indentified as requiring further research.
- **Should further combustion research focus on pure pyrolysis oils? What are the critical research needs in combustion? Scale? To what extent is blending of pyrolysis oil acceptable? Required? With which conventional fuel is blending best accomplished? Is emulsification with diesel fuel a suitable approach?**

Pyrolysis Oil Combustion Research

Fernando Preto
Natural Resources Canada

CanmetENERGY Research Tunnel Furnace

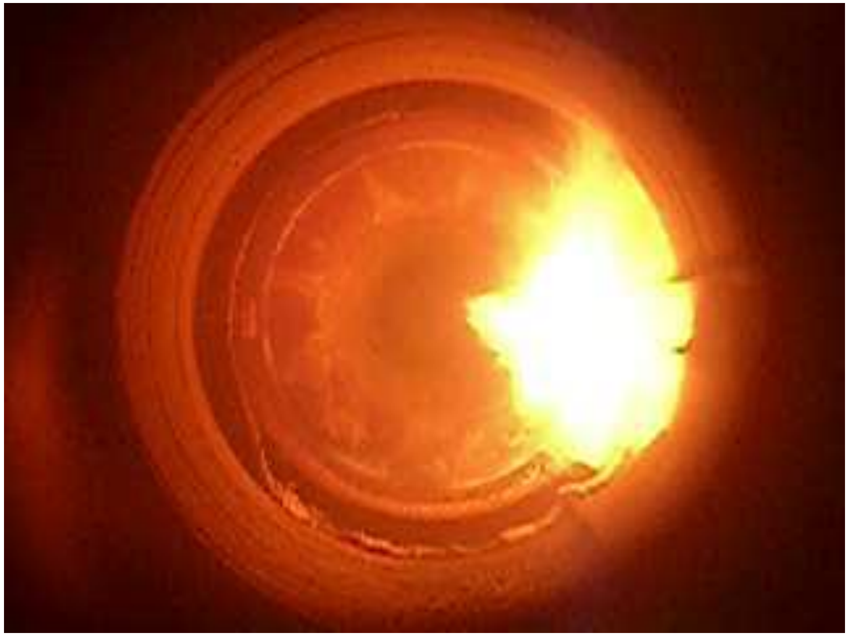


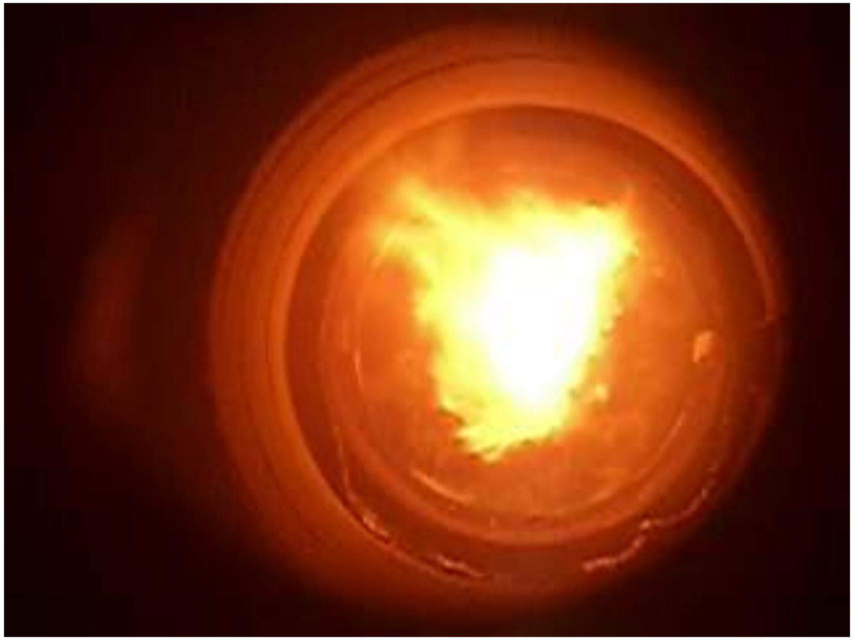
Pyrolysis Oil Analyses

Bio-oil	Water Content (wt%)	Viscosity @ 70C (cSt)	Density @ 25C (g/cm^3)	Acid Content (weak) dry wt%	HHV (MJ/kg)	Acetone THF Insolubles (wt%)
Tote 1(#1)	**24.96**	16.97	1.32	7.40	**17.18**	0.27
Tote 2(#2)	**31.17**	4.86	1.20	10.50	**14.63**	0.80

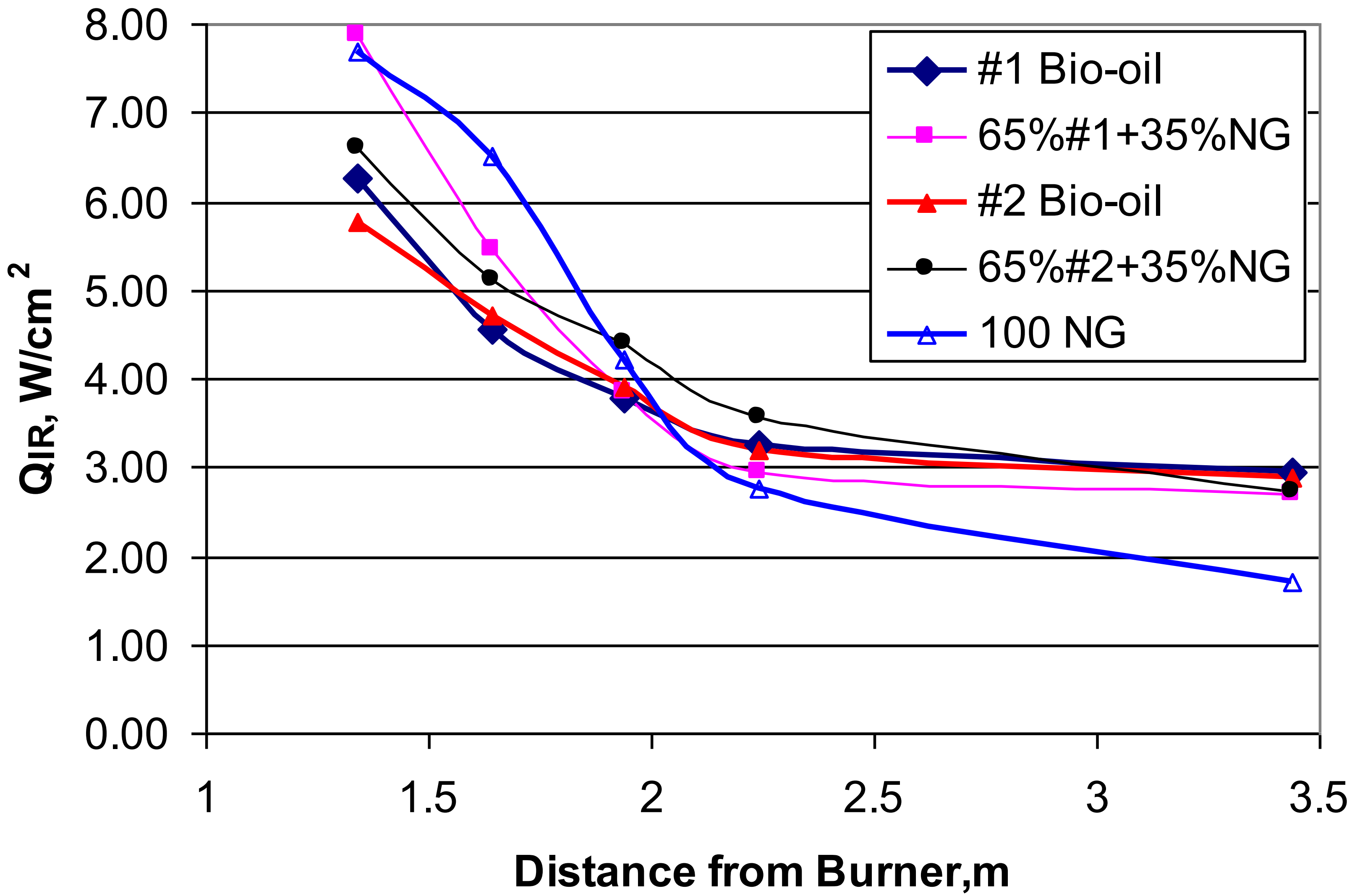
Bio-oil		Viscosity @ 40C (cSt)	Density @ 15C g/cm^3	C, wt%	H, wt%	N, wt%	S, wt%	Ash wt %	HHV MJ/kg
#1		**510.3**	**1.25**	**47.12**	**7.78**	**0.23**	**< 0.05**	**.06**	**18.97**
#2		**817.3**	**1.27**	**52.0**	**6.78**	**0.23**	**< 0.05**	**.70**	**20.91**

Variation In Bio-oil Properties In Some Cases Required Nozzle Adjustments





Radiation Flux Measurements



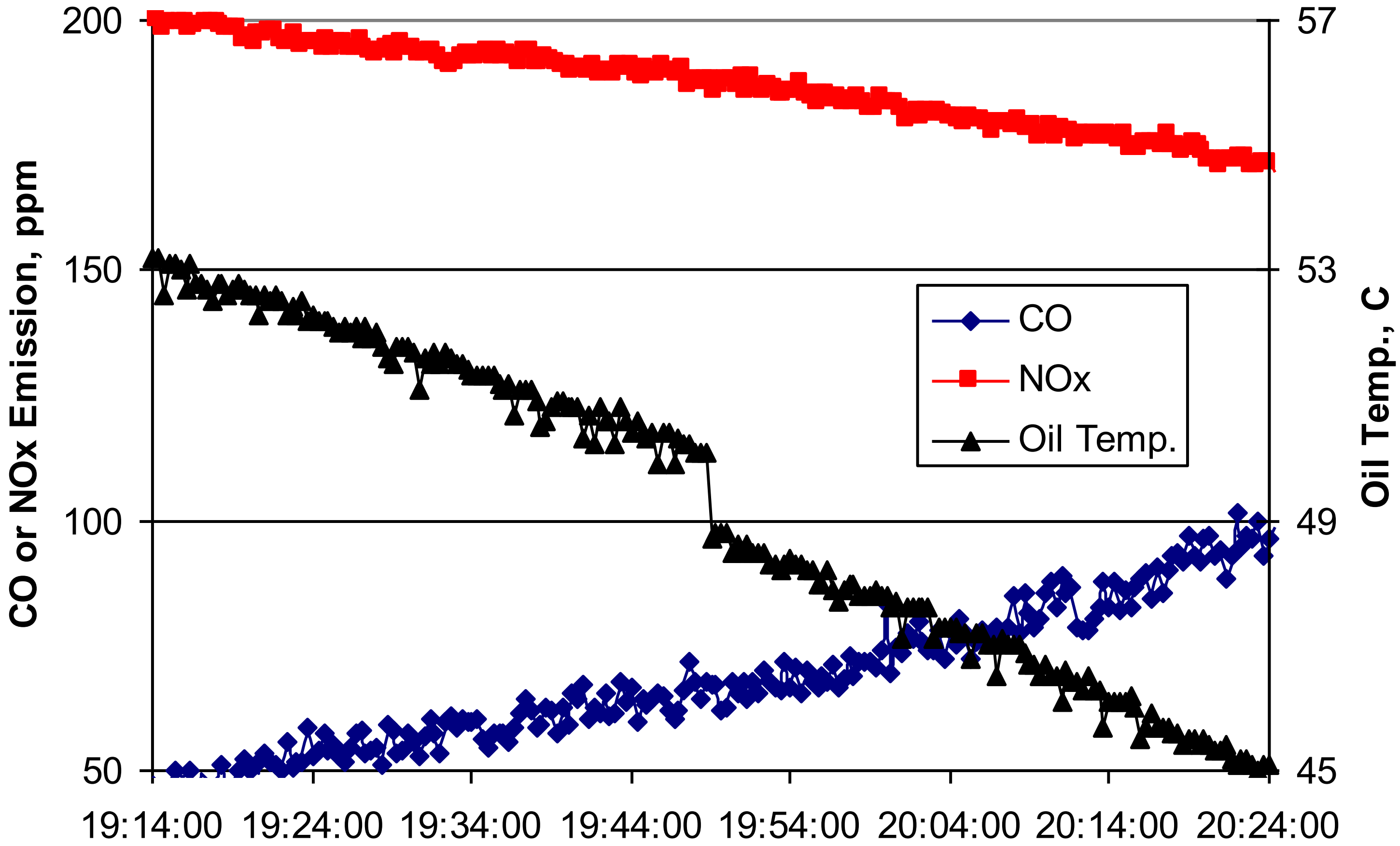
#1 Bio-oil combustion results

Name	Unit	100%#1 (1)	100%#1 (2)	65%#1	90%#1	80%#1	50%#1	100% NG
Bio oil Feed rate	Kg/h	68.1	68.1	44.3	61.3	54.5	34	0
Oil temp.	C	53.3	50	53.5	53.4	50.4	52.9	0
NG Feed rate	Kg/h	0	0	7.7	2.2	4.4	11	22
Heat input	MJ/h	1292	1292	1250	1280	1268	1230	1170
Atomising Air Flow rate	Kg/h	34.6	34.1	33.0	33.7	33.8	33.0	32.5
Combustion Air Flow rate	Kg/h	697.6	715.2	669.7	690.1	684.1	652.1	421.1
Combustion Air Temperature	C	116.7	45.5	119.8	119.9	120.4	121.2	121.3
Stack gas, O2	%	4.33	4.63	4.55	4.54	4.54	4.53	4.24
Stack gas, CO	Ppm	45.4	87.4	38.6	50.0	46.5	48.8	15.5
Stack gas, NO	Ppm	458.7	269.8	198.0	180	185.6	152.8	61.3
Stack gas,PM	Mg/m^3	77	78	47	-	-	-	-

#2 Bio-oil combustion results

Name	Unit	100%#2	65%#2	90%*2	90%#2	80%#2	50%#2
Bio oil Feed rate	Kg/h	80	52	72	72	64	40
Oil temp.	C	50.8	48.8	52.6	59.8	49.4	49.7
NG Feed rate	Kg/h	0	7.7	2.2	2.2	4.4	11
Heat input	MJ/h	1673	1497	1622	1622	1572	1421
Atomising Air Flow rate	Kg/h	48.5	31.9	35.3	35.9	33.8	26.1
Combustion Air Flow rate	Kg/h	665.1	662.9	667.3	687.1	670.5	641.7
Combustion Air Temperature	C	115.5	44.5	86.6	90.2	66.3	40.2
Stack gas, O2	%	4.47	4.64	4.05	4.55	4.4	4.57
Stack gas, CO	Ppm	106.3	30.8	146.5	87.6	68.1	14.9
Stack gas, NO	Ppm	156	152	141	144	151	122
Stack gas,PM	Mg/m^3	242	182	-	-	-	-

Effect of #1 Bio-oil Temperature on CO and NOx



CO and NOx emission variation due to Oil Temperature of the Blend(65%#1, 35%NG)

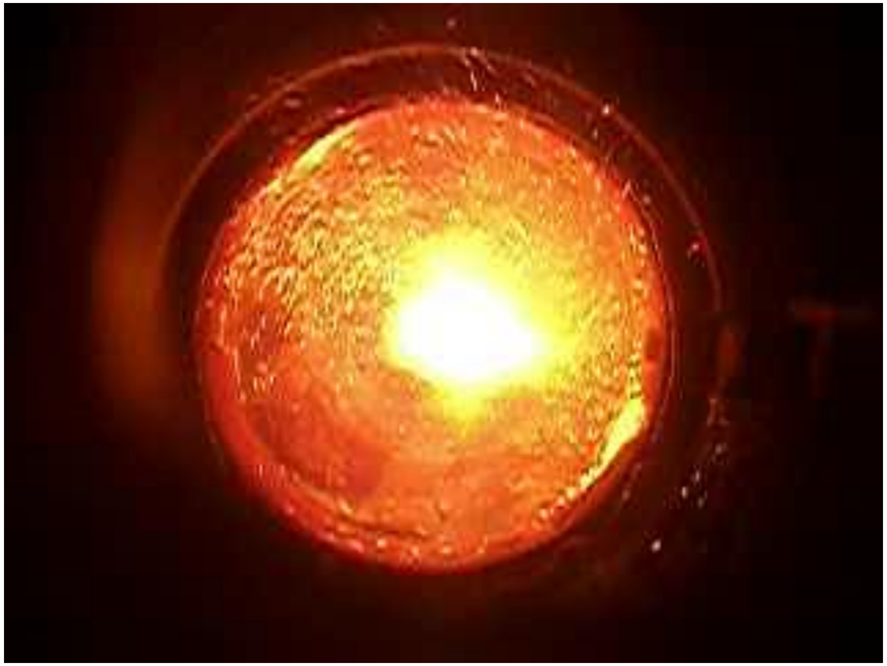
Effect of Combustion Air Temperature

(1)- Tote #1 comb air temp 117 C

(2)- Tote #1 comb air temp 46 C

Effect of Bio-Oil Temperature

Bio-oil (#1) Temperature 54C **45C**



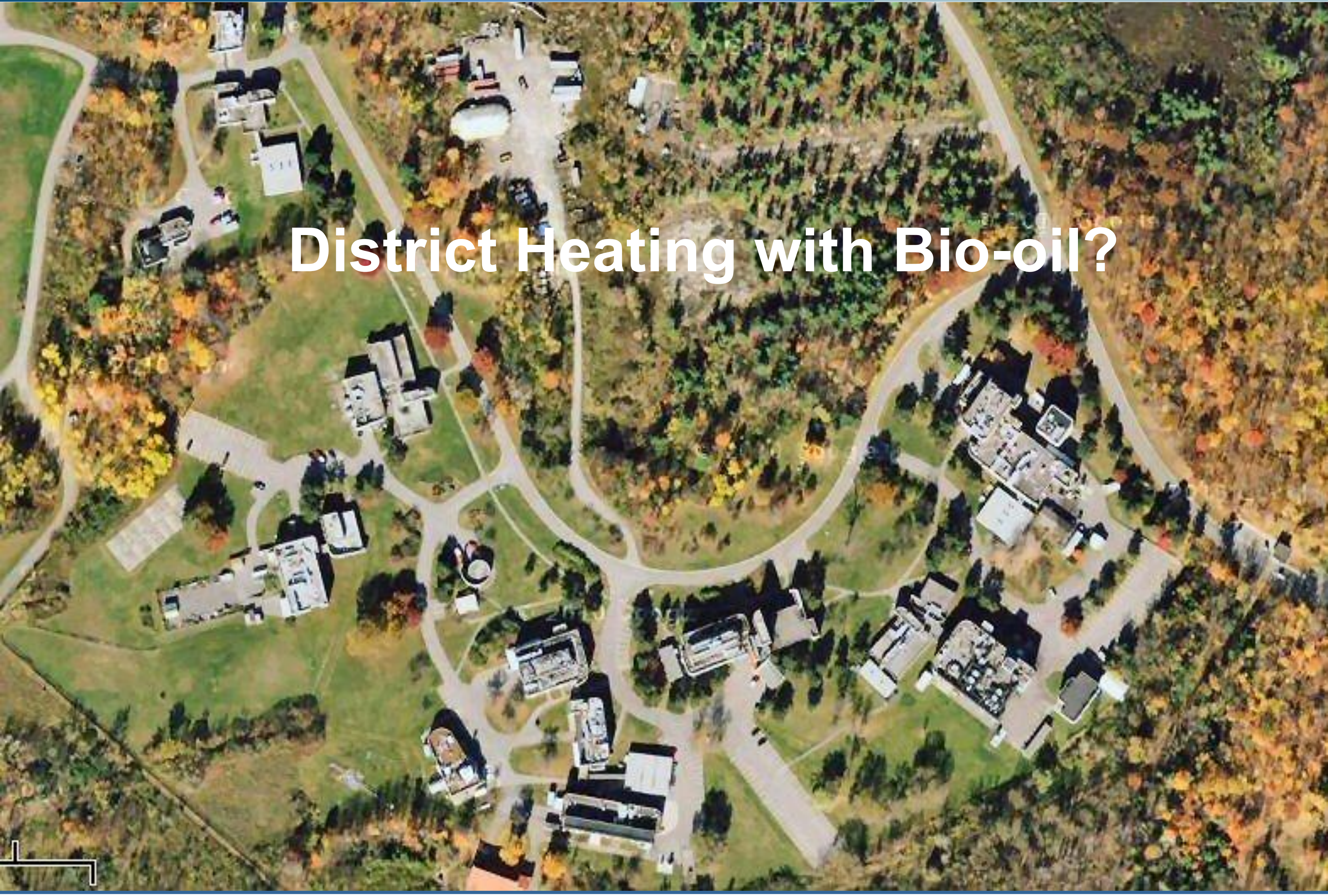
Co-firing with 35% Natural Gas

Cold Start Attempts (Bio-oil #2)

Using Ignitor (Comb. Air Temperature 30C   abd 85C)

Natural Gas pilot support – flame extinguished within 1 minute

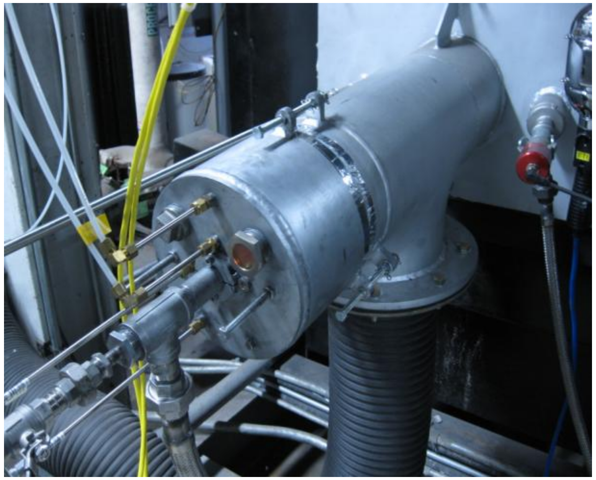
District Heating with Bio-oil?



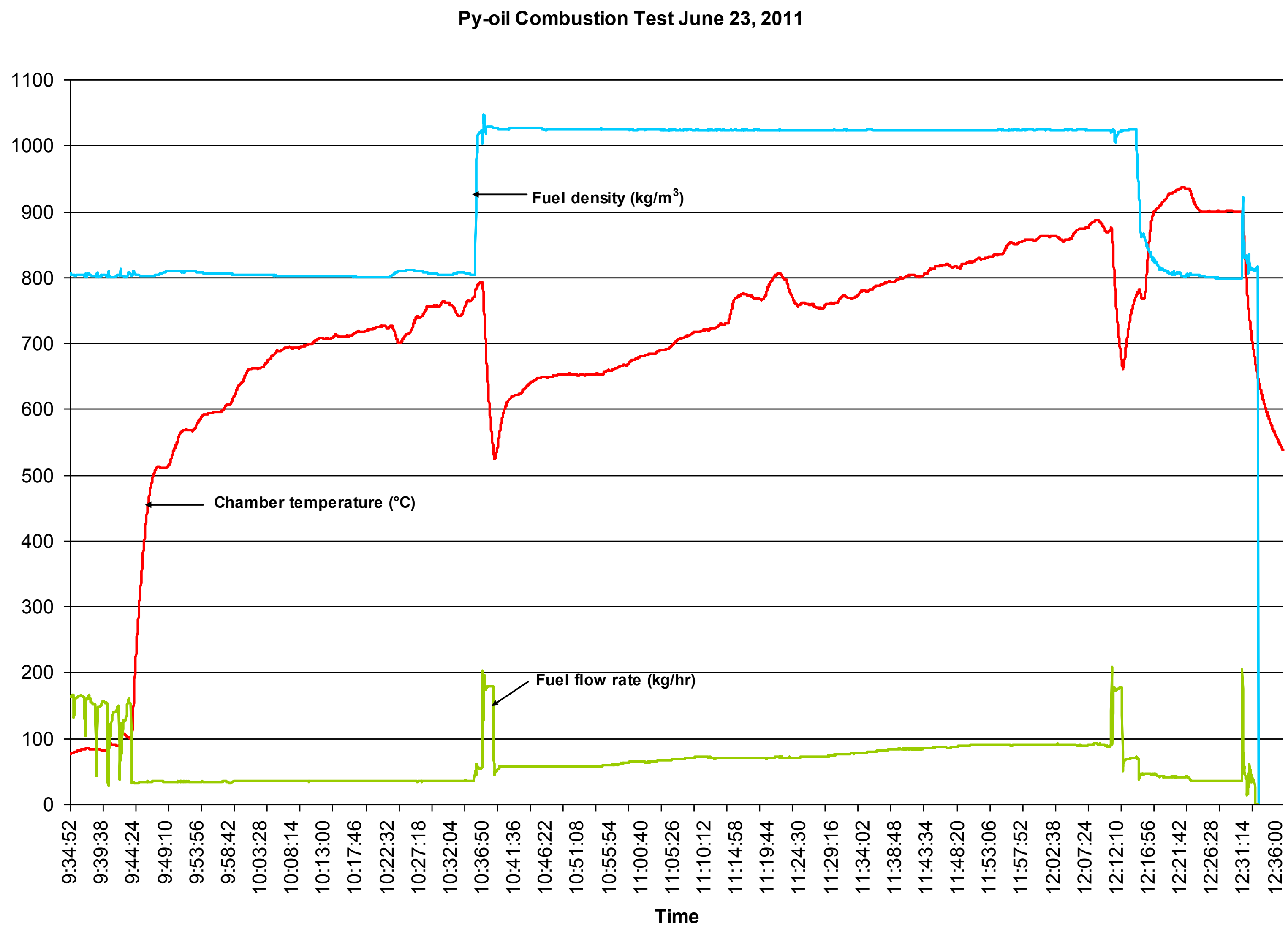
Commercial Combustion of Bio-oil

- Project objective
  - Develop automated stand-alone system for bio-oil combustion as replacement for oil/natural gas boilers
- Partners
  - CanmetENERGY
    - Combustion Expertise incl. bio-oil
  - Ensyn Technologies
    - Production & handling of bio-oil oil
  - Brais, Malouin and Associates
    - Power boiler, petrochem and modeling expertise

Facility Development

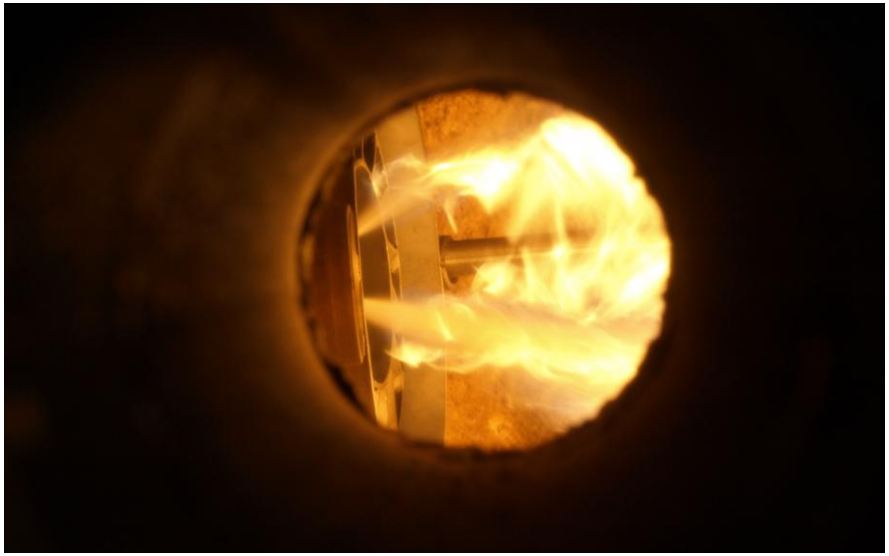


Combustion Test



Further Development

- Nozzle design
- Controls incl. flame sensor location
- Ignition Control
- Flame stability
- Cold Start



CanmetENERGY
Leadership in ecoInnovation

Challenges – Corrosivity

- Corrosion studies at ORNL have shown that raw pyrolysis oil is very corrosive to carbon steel and other alloys with relatively low chromium content. Stress corrosion cracking samples of carbon steel and several low alloy steels developed through-wall cracks after a few hundred hours of exposure at 50°C. Chemical analyses have identified the carboxylic acid compounds as well as the other organic components which are primarily aromatic hydrocarbons.
- **Are further corrosion studies necessary or is it enough to specify plastic or stainless? Can pyrolysis oil be effectively neutralized?**

Challenges – Comfort and Toxicity

- If pyrolysis oils is going to be used for wide-spread heating issues like comfort and toxicity will have to be addressed. Further work is required to develop procedures for dealing with spills. Detailed toxicological data is required for exposure to liquids and vapours. A number of MSDS for pyrolysis oils are available, however the experiences and claims from commercial producers need to be assessed and incorporated into a comprehensive MSDS.
- **How can spills be remediated?**
  Is there a procedure for resolving MSDS conflicts?

Challenges – Standards and Regulations

- The IEA Bioenergy Task 34 collaboration has development of norms and standards including establishment of standards for bio-oil utilization. Included in this is having a CAS number issued for fast pyrolysis bio-oil (RN 1207435-39-9) and supporting an Ensyn-led effort to develop ASTM Standard D7544-09.
- **What additional standards are required for infrastructure development? Are there local regulatory requirements which must be met?**

Designation: D7544 – 10

Standard Specification for Pyrolysis Liquid Biofuel[1]

This standard is issued under the fixed designation D7544; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This specification covers a pyrolysis liquid biofuel produced from biomass intended for use in industrial burners equipped to handle these types of fuels. This type of biofuel is not intended for use in residential heaters, small commercial boilers, engines, or marine applications.

D240 Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter
D396 Specification for Fuel Oils
D445 Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)
D482 Test Method for Ash from Petroleum Products

TABLE 1 Detailed Requirements for Pyrolysis Liquid Biofuels

Property	Test Method	Specification	Units
Gross Heat of Combustion	D240	15 min	MJ/kg
Water Content	E203	30 max	mass %
Pyrolysis Solids Content	D7579	2.5 max	mass %
Kinematic Viscosity at 40°C	D445[A]	125 max	mm^2/s
Density at 20°C	D4052	1.1–1.3	kg/dm^3
Sulfur Content	D4294	0.05 max	mass %
Ash Content	D482	0.25 max	mass %
pH	E70	Report	...
Flash Point	D93, Procedure B	45 min	°C
Pour Point	D97	–9 max	°C

[A] Without filtering.

IEA Bioenergy Task 34 is evaluating Pyrolysis Oil Designations:

E.G. **Grade B: Bio-oil for power prod. in medium speed stationary diesel engines TAN <15**
Grade D: Light fuel oil (<0.2 wt% solids and ash <0.1%)
Grade G: Heavy fuel Oils (ASTM D7544)

Contact:

Fernando Preto
CanmetENERGY
Natural Resources Canada
preto@nrcan.gc.ca
Tel: 613-996-5589