Solid Fuel Characterisation

- methods, equipment and characteristics

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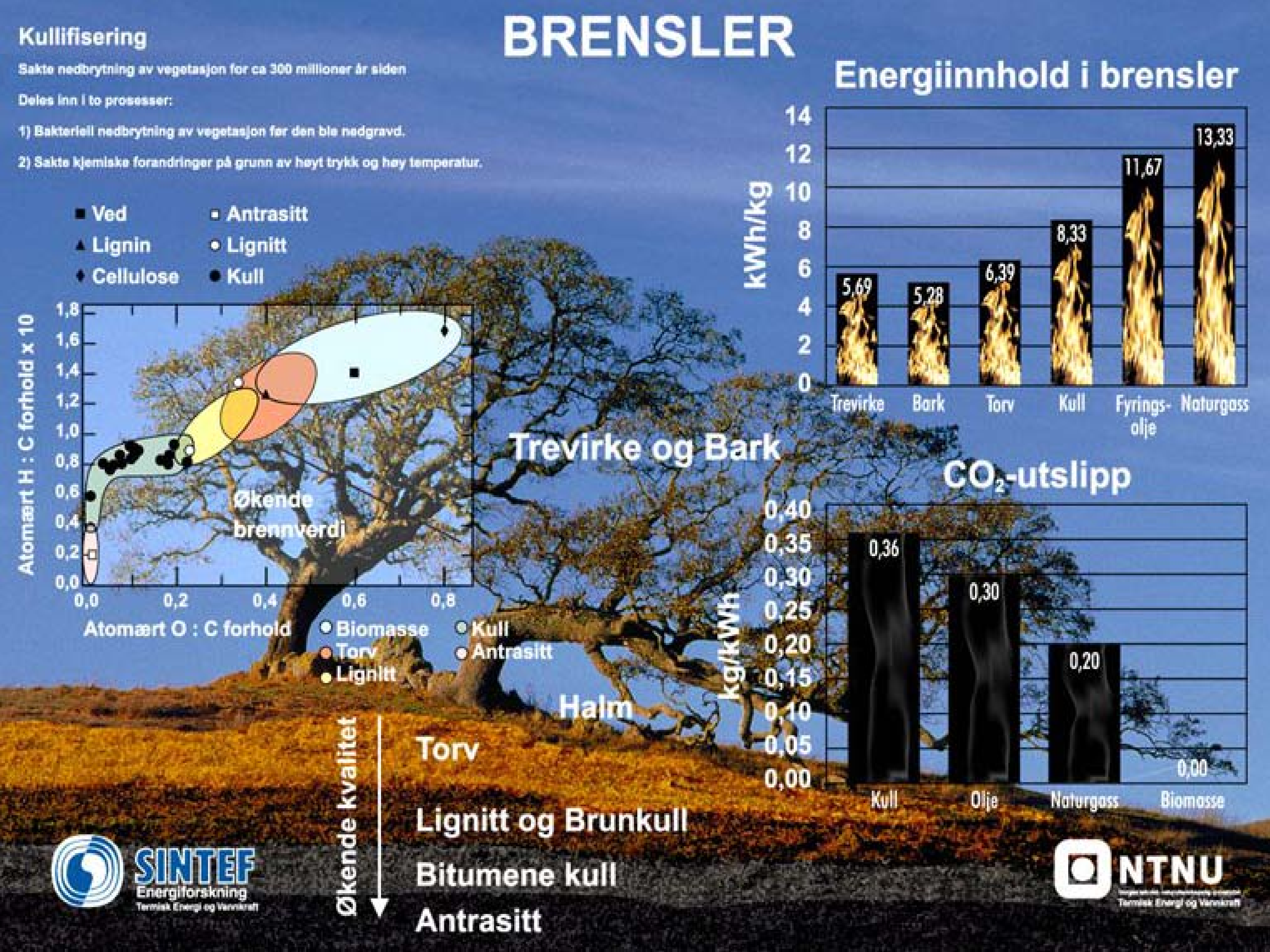
Biomass
- Physical and chemical properties

Standards
- ISO
- ASTM
- DIN
- CEN

Fuel preparation
- Grinding/milling
- Sieving
- Drying & storage

Characterization methods
- Proximate analyses
- Ultimate (elemental) analyses
- Heating value
- Ash melting

Equipment
- Mill
- Drying chamber
- Desiccator
- Muffle furnace
- Elemental analyser
- Bomb Calorimeter
- Ash melting microscopy
- Thermogravimetric Analyser (TGA)
- Differential Scanning Calorimeter (DSC)


BRENSLER
Kullifisering
Sakte nedbrytning av vegetasjon for ca 300 millioner år siden
Deles inn i to prosesser:
1) Bakteriell nedbrytning av vegetasjon før den ble nedgravd.
2) Sakte kjemiske forandringer på grunn av høyt trykk og høy temperatur.
Ved
Lignin
Cellulose
Antrasitt
Lignitt
Kull
Atomært H : C forhold x 10
1,8
1,6
1,4
1,2
1,0
0,8
0,6
0,4
0,2
0,0
0,0
0,2
0,4
0,6
0,8
Atomært O : C forhold
Økende brennverdi
Biomasse
Kull
Torv
Antrasitt
Lignitt
Energiinnhold i brensler
kWh/kg
14
12
10
8
6
4
2
0
5,69
5,28
6,39
8,33
11,67
13,33
Trevirke
Bark
Torv
Kull
Fyrings-olje
Naturgass
Trevirke og Bark
CO2-utslipp
kg/kWh
0,40
0,35
0,30
0,25
0,20
0,15
0,10
0,05
0,00
0,36
0,30
0,20
0,00
Kull
Olje
Naturgass
Biomasse
Halm
Torv
Lignitt og Brunkull
Bitumene kull
Antrasitt
Økende kvalitet
SINTEF
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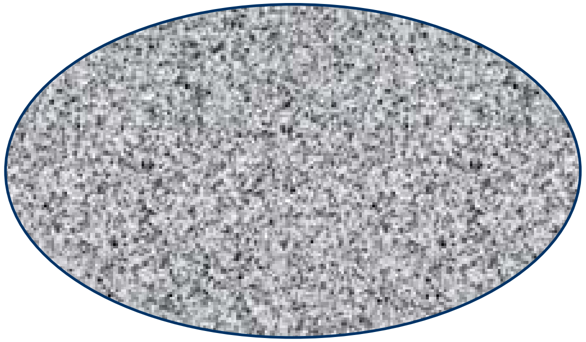
NTNU
Termisk Energi og Vannkraft

Biomass

Virgin biomass – wood logs

Refined biomass – charcoal



Refined biomass – pellets and wood powder

Refined biomass – briquettes

Biomass

- **Softwoods**: evergreen trees with needles
- **Hardwoods**: broad-leafed trees that shed their leaves at the end of each growing season
- **Bark** – different structure – sponglike – irregular pattern. Bark contain more resin and more ash than wood
- **Agricultural residues**
- **Grasses**
- **Animal residues**: Manure
- **Charcoal**: made by heating the wood in the absence of air

Birch (Betula Verrucosa)

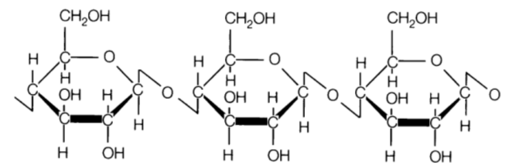
Spruce (Picea Abies)

Pine (Pinus Silvestris)

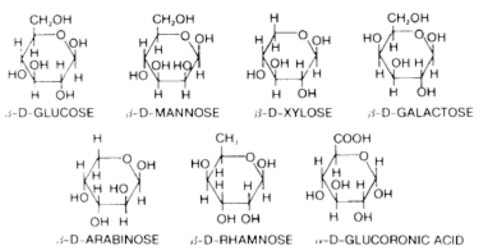
Chemical composition of wood

- **Cellulose** ($C_6H_{10}O_5$) is a condensed polymer of glucose. The fiber walls consist mainly of cellulose and represents 40-45% of the dry weight of wood
- **Hemicellulose** consist of various sugars other than glucose that encase the cellulose fibers and represent 20-35% of the dry weight of wood
- **Lignin** ($C_{40}H_{44}O_6$) is a nonsugar polymer that gives strength to the wood fiber, accounting for 15 to 30% of the dry weight of wood
- **Resins** (extractives) account only for a few percent of the dry weight of wood, but 20 to 40% in bark
- **Ash**: 0.2 to 1% of mainly calcium, potassium, magnesium, manganese and sodium oxides, and lesser amounts of other oxides of iron, aluminum, etc. The ash content in bark is typically 1 to 3%

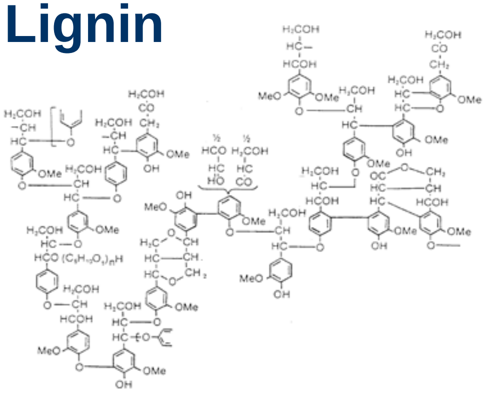
Cellulose



Hemicellulose



Lignin



Chemical composition of wood

Table 2.1 Chemical composition of some selected wood species [Wenzl (1970)]

Species	Cellulose	Hemicelluloses	Lignin	Extractives
Softwoods				
Scandinavian Spruce	43	27	29	1.8
Scandinavian Pine	44	26	29	5.3
Douglas Fir	39	23	29	5.3
Scots Pine	40	25	28	3.5
Hardwoods				
Scandinavian Birch	40	39	21	3.1
Silver Birch	41	30	22	3.2
American Beech	48	28	22	2.0

Physical and chemical properties

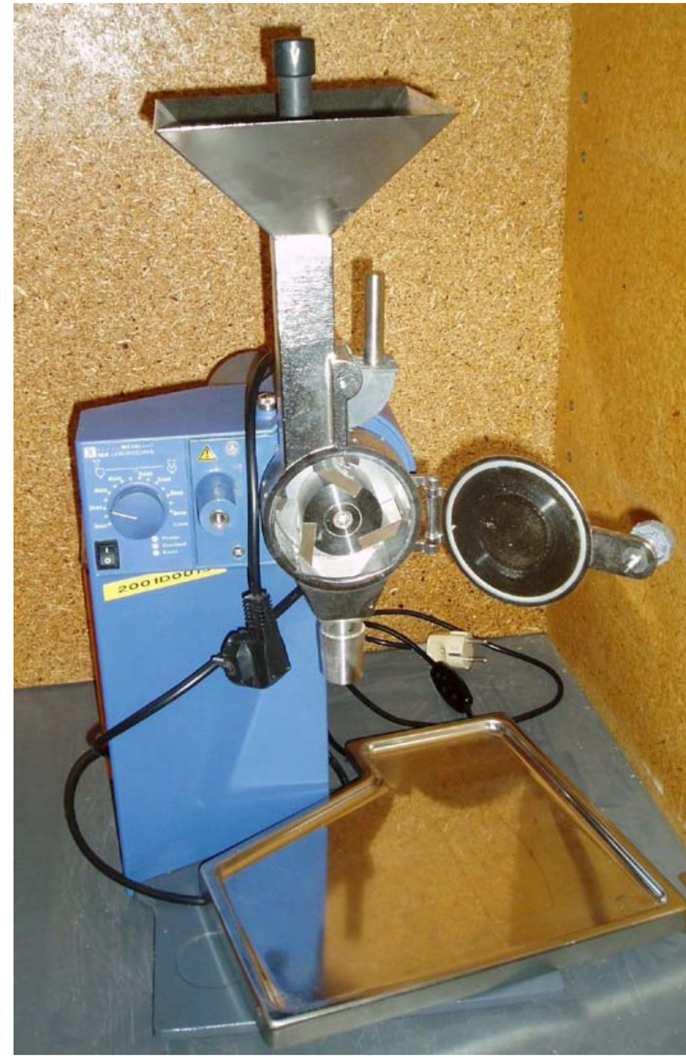
Characteristics	Effects
* moisture content	* storage durability and dry-matter losses, NCV, self-ignition, plant design
* NCV, GCV	* fuel utilisation, plant design
* volatiles	* thermal decomposition behaviour
* ash content	* dust emissions, ash manipulation, ash utilisation/ disposal, combustion technology
* ash-melting behaviour	* operational safety, combustion technology, process control system
* fungi	* health risks

Physical and chemical properties

Characteristics	Effects
* bulk density	* fuel logistics (storage, transport, handling)
* particle density	* thermal conductance, thermal decomposition
* physical dimension, form, size distribution	* hoisting and conveying, combustion technology, bridging, operational safety, drying, formation of dust
* fine parts (wood pressings)	* storage volume, transport losses, dust formation
* abrasion resistance (wood pressings)	* quality changes, segregation, fine parts

- ISO standard (http://www.iso.com/)
  - Insurance Service Office
- ASTM standard (http://www.astm.org/)
  - ASTM International
- DIN standard (http://www2.din.de/)
  - Deutches Institut für Normung
- CEN standard (http://www.cenorm.be/)
  - The European Committee for Standardization

Grinding/milling



Sieving

Drying & storage

Drying chamber

Desiccator

Proximate analyses

- **Determination of volatile matter content (VM):**
  The sample is heated ("carbonised") in a covered crucible to 950ºC and kept at this temperature for 7 minutes.

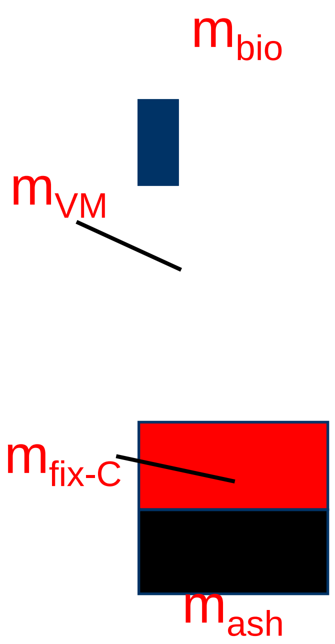
$$X_{VM} = 100\% \cdot m_{VM}/m_{bio}$$

- **Determination of ash content:**
  The sample is burned in an 'open' crucible to 600ºC and held at this temperature for 4-6 hours.

$$X_{ash} = 100\% \cdot m_{ash}/m_{bio}$$

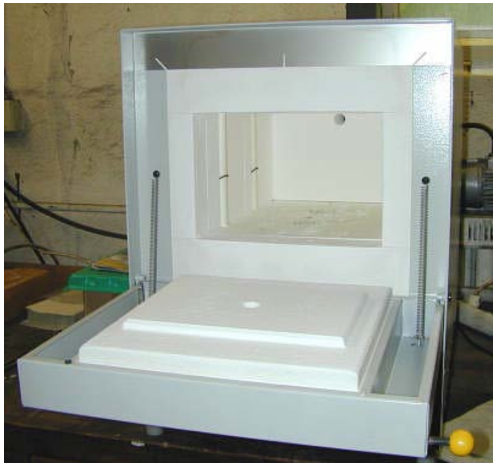
- **Determination of fix-C content:**
  The fixed carbon content is defined as:

$$X_{fix\text{-}C} = 100\% - (X_{VM} + X_{ash})$$



Proximate analyses

Muffle furnace



Crucible

	Moisture	VM	Ash
Standard	ASTM E871	ASTM E872	ASTM D1102
Sample mass	50 g	1 g	2 g
Sieve size	----	1 mm	0.5 mm
Temperature	103°C ± 2°C	950°C	580-600°C
Holding time	24 h	7 min	4 h
Crucible size	----	25 mm < D < 35 mm	D = 44 mm
	----	30 mm < H < 35 mm	H = 22 mm

Proximate analyses

	Proximate analyses (wt%)		
	VM	Fix C	Ash
Birch	87.4	12.4	0.20
Pine	85.0	14.7	0.31
Spruce	85.4	14.4	0.26
Forest residues (Sweden)	79.3	19.37	1.33
Forest residues (Finland)	74.1	21.85	4.05
Salix	79.9	18.92	1.18
Bark from spruce	75.2	22.46	2.34
Bark from pine	73.0	25.30	1.70
Wheat straw (Denmark)	77.7	17.59	4.71
Barely straw (Finland)	76.1	18.02	5.88
Rape seed	79.2	17.94	2.86
Flax	78.8	18.27	2.93
Reed canary grass	73.5	17.65	8.85
Kenaf (Italy)	79.4	16.97	3.63

Ultimate (elemental) Analyses

- The sample is burned in a combustion chamber in O_2-atmosphere with helium (He) as carrier gas.
- Combustion gases are CO_2, H_2O, NO, NO_2, SO_2, SO_3 and N_2.
- SO_3, NO and NO_2 are reduced at copper contact to SO_2 and N_2. H_2O, SO_2 and CO_2 are captured in different adsorption columns.
- N_2 is not captured by the columns and is detected first by a thermal conductivity detector (TCD).
- H_2O, SO_2, CO_2 will be released consecutively and sent to the TCD.
- Mass-percentage is determined integrally.
- By known sample weight the C, H, N and S content can be determined.

Ultimate (elemental) Analyses

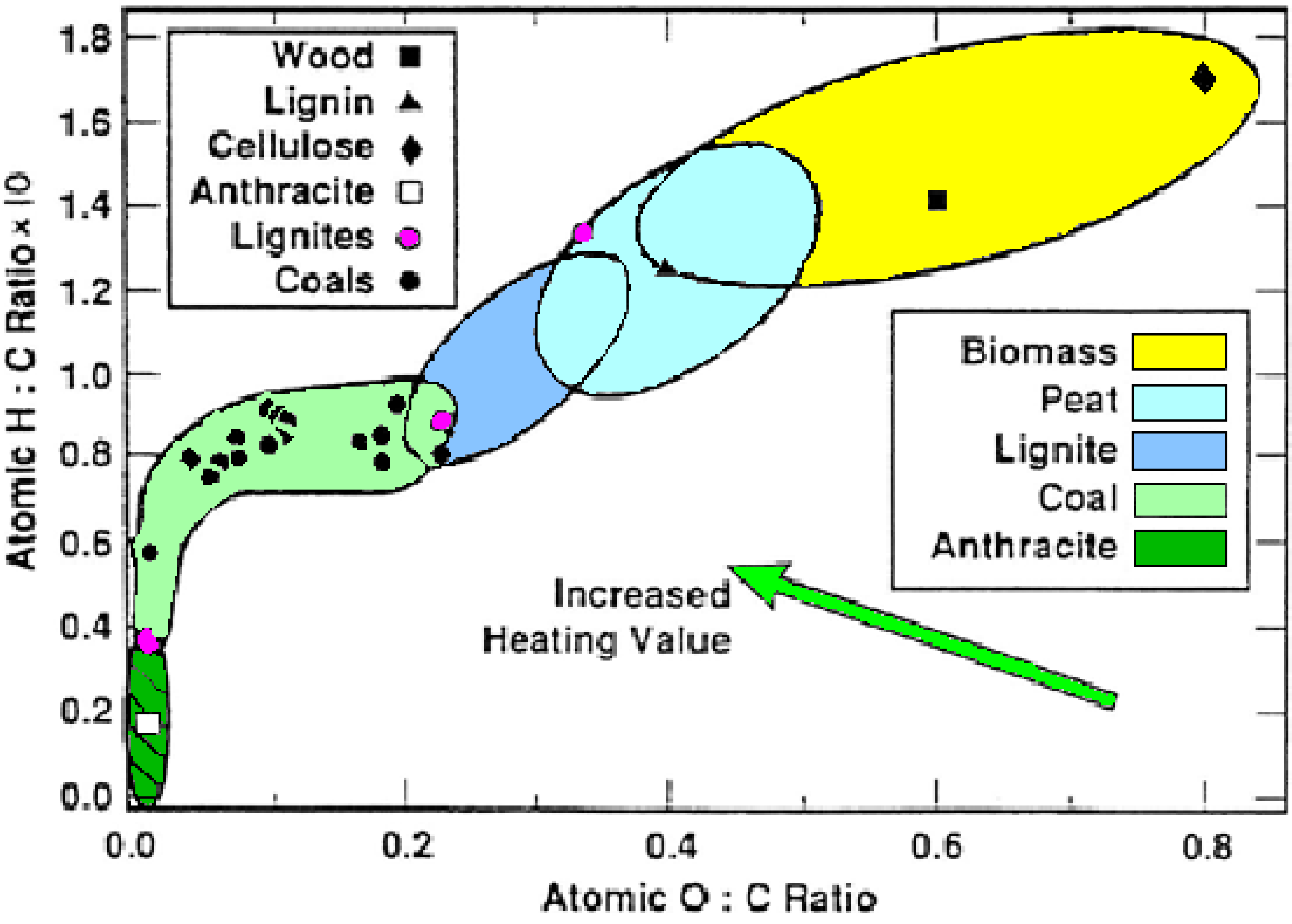
	Standard
Carbon, hydrogen	ASTM E 777
Nitrogen	ASTM E 778
Sulphur	ASTM E 775
Chlorine	ASTM E 776
Oxygen	by difference

Vario Macro (Elementar)

Ultimate (elemental) Analyses

	Proximate analyses (wt%)			Ultimate analyses (wt%)					
	VM	Fix C	Ash	C	H	N	O	S	Ash
Birch	87.4	12.4	0.20	48.07	6.00	0.17	45.56	< 0.05	0.20
Pine	85.0	14.7	0.31	49.41	6.11	0.11	44.07	< 0.05	0.31
Spruce	85.4	14.4	0.26	48.91	6.02	0.12	44.65	< 0.05	0.26
Forest residues (Sweden)	79.3	19.37	1.33	51.30	6.10	0.40	40.85	0.02	1.33
Forest residues (Finland)	74.1	21.85	4.05	51.00	5.80	0.90	38.21	0.04	4.05
Salix	79.9	18.92	1.18	49.70	6.10	0.40	42.59	0.03	1.18
Bark from spruce	75.2	22.46	2.34	49.90	5.90	0.40	41.43	0.03	2.34
Bark from pine	73.0	25.30	1.70	52.50	5.70	0.40	39.65	0.03	1.70
Wheat straw (Denmark)	77.7	17.59	4.71	47.30	5.87	0.58	41.49	0.07	4.71
Barely straw (Finland)	76.1	18.02	5.88	46.20	5.70	0.60	41.54	0.08	5.88
Rape seed	79.2	17.94	2.86	48.10	5.90	0.80	42.13	0.21	2.86
Flax	78.8	18.27	2.93	49.10	6.10	1.30	40.45	0.12	2.93
Reed canary grass	73.5	17.65	8.85	45.00	5.70	1.40	38.91	0.14	8.85
Kenaf (Italy)	79.4	16.97	3.63	46.60	5.80	1.00	42.83	0.14	3.63

Van Krevlen Diagram



Heating value

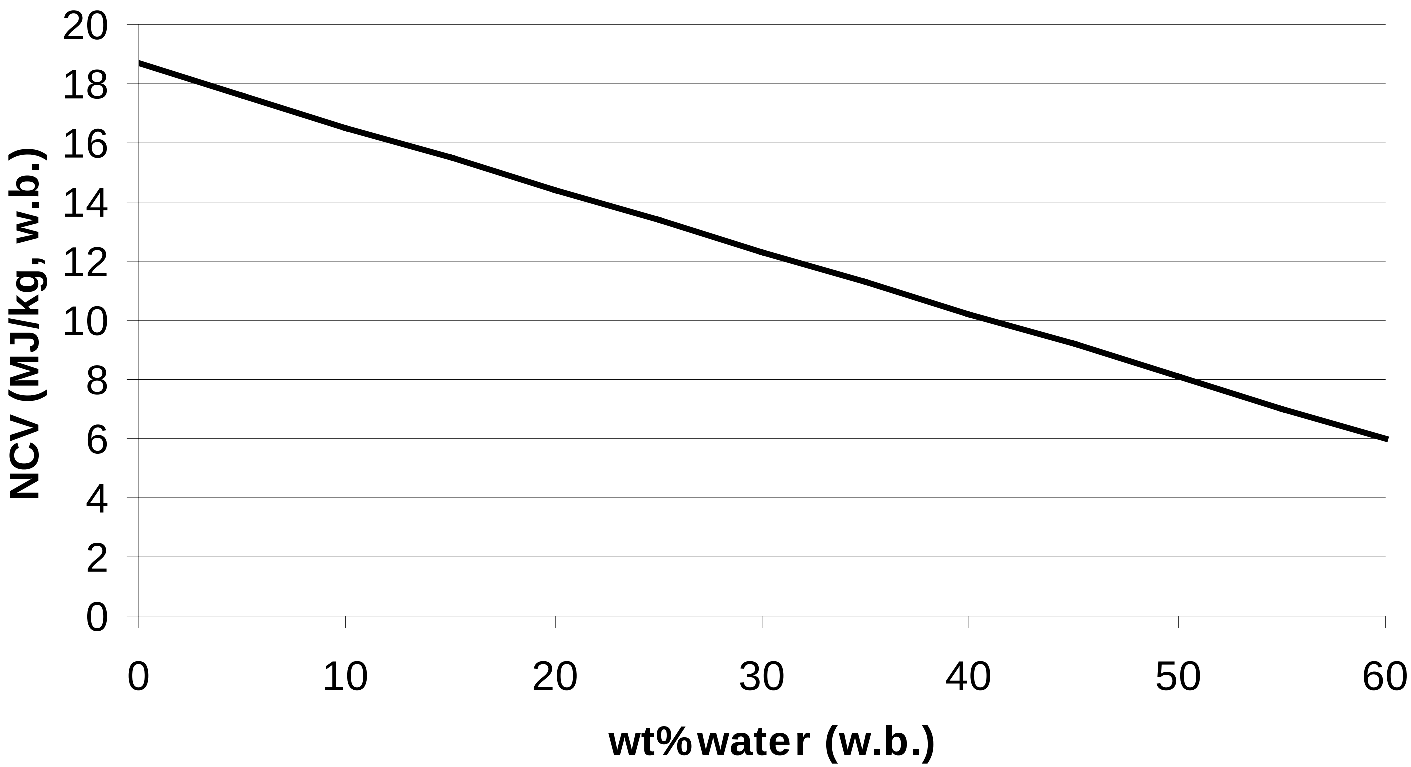
- Higher Heating Value (HHV) is obtained by combustion of the sample in an adiabatic bomb calorimeter. The HHV is calculated from measured temperature increase in the adiabatic system.
- Lower Heating Value (LHV) can be calculated from HHV by taking into account the hydrogen content of the sample
- Effective Heating Value (EHV) can be calculated from LHV by taking into account the moisture content in the sample
- HHV can be calculated when the elemental composition is known:

$$HHV = 0.3491 \cdot \%C + 1.1783 \cdot \%H + 0.1005 \cdot S\% - 0.0151 \cdot N\% - 0.1034 \cdot O\% - 0.0211 \cdot ash\% \quad [MJ/kg]$$

Fuel composition and heating values

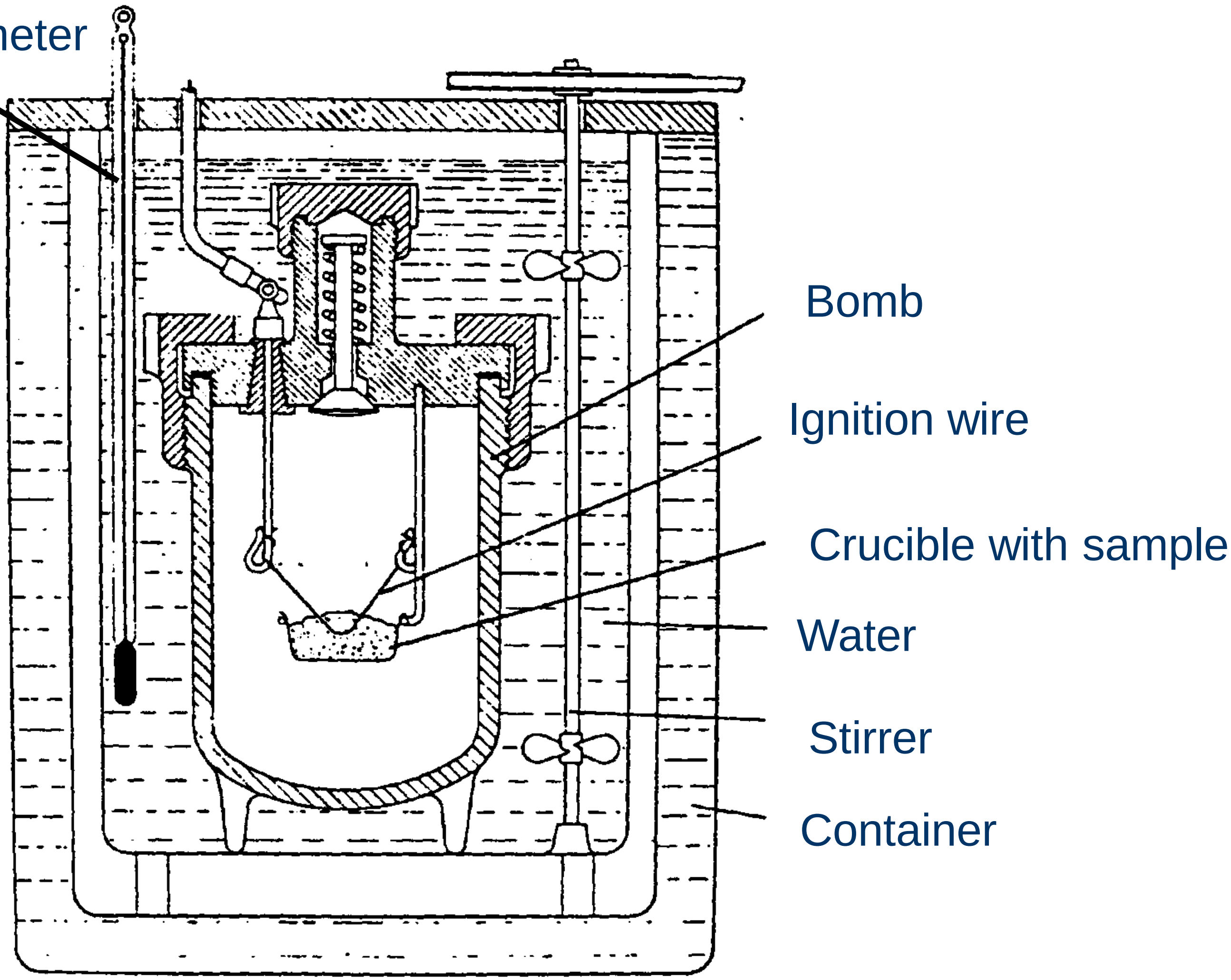
$$\text{EHV} = \text{UHV} \cdot \left(1 - \frac{w}{100}\right) - H_{evap,H_2O} \cdot \frac{w}{100} - H_{evap,H_2O} \cdot \frac{h}{100} \cdot \frac{M_{H_2O}}{M_{H_2}} \cdot \left(1 - \frac{w}{100}\right) \quad \left[\text{MJ/kg, wet basis } (\mathbf{w.b.})\right]$$

w	moisture content of the fuel in wt% (w.b.)	$H_{evap,\ H2O}$ = Heat of evaporation for water = 2.444 MJ/kg
h	hydrogen content of the fuel in wt% (d.b.)	M_{H2O}, M_{H2}: molecular weights



NCV as a function of wt% moisture (w.b.) for a fuel composition of 50 wt% C, 6 wt% H, and 44 wt% O (d.b.).

Heating value



Heating value

Bomb calorimeter - Principle

Heating value

Examples

	Proximate analyses (wt%)			Ultimate analyses (wt%)						HHV (MJ/kg)
	VM	Fix C	Ash	C	H	N	O	S	Ash	
Birch	87.4	12.4	0.20	48.07	6.00	0.17	45.56	< 0.05	0.20	19.19
Pine	85.0	14.7	0.31	49.41	6.11	0.11	44.07	< 0.05	0.31	19.65
Spruce	85.4	14.4	0.26	48.91	6.02	0.12	44.65	< 0.05	0.26	19.56
Forest residues (Sweden)	79.3	19.37	1.33	51.30	6.10	0.40	40.85	0.02	1.33	20.67
Forest residues (Finland)	74.1	21.85	4.05	51.00	5.80	0.90	38.21	0.04	4.05	20.54
Salix	79.9	18.92	1.18	49.70	6.10	0.40	42.59	0.03	1.18	19.75
Bark from spruce	75.2	22.46	2.34	49.90	5.90	0.40	41.43	0.03	2.34	19.83
Bark from pine	73.0	25.30	1.70	52.50	5.70	0.40	39.65	0.03	1.70	20.95
Wheat straw (Denmark)	77.7	17.59	4.71	47.30	5.87	0.58	41.49	0.07	4.71	18.94
Barely straw (Finland)	76.1	18.02	5.88	46.20	5.70	0.60	41.54	0.08	5.88	18.68
Rape seed	79.2	17.94	2.86	48.10	5.90	0.80	42.13	0.21	2.86	19.33
Flax	78.8	18.27	2.93	49.10	6.10	1.30	40.45	0.12	2.93	20.04
Reed canary grass	73.5	17.65	8.85	45.00	5.70	1.40	38.91	0.14	8.85	18.37
Kenaf (Italy)	79.4	16.97	3.63	46.60	5.80	1.00	42.83	0.14	3.63	18.58

Biomass & waste components

Sample	Proximate Analysis			Ultimate Analysis [20,30,40]						HHV (MJ/kg)
	VM (wt%)	Fix-C (wt%)	Ash (wt%)	C (wt%)	H (wt%)	O[a] (wt%)	N (wt%)	S (wt%)	Cl (wt%)	
Cellulosic fraction:										
Newspaper	88.5	10.5	1.0	52.1	5.9	41.86	0.11	0.03	n.a.	19.3
Cardboard	84.7	6.9	8.4	48.6	6.2	44.96	0.11	0.13	n.a.	16.9
Recycled paper	73.6	6.2	20.2[b] 22.4[c]	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	13.6
Glossy paper	67.3	4.7	28.0[b] 42.7[c]	45.6	4.8	49.41	0.14	0.05	n.a.	10.4
Spruce	89.6	10.2	0.2	47.4	6.3	46.2	0.07	n.a.	n.a.	19.3
Plastics:										
HDPE	100.0	0.0	0.0	86.1	13.0	0.90	n.a.	n.a.	n.a.	46.4
LDPE	100.0	0.0	0.0	85.7	14.2	0.05	0.05	0.00	n.a.	46.6
PP	100.0	0.0	0.0	86.1	13.7	0.20	n.a.	n.a.	n.a.	46.4
PS	99.8	0.2	0.0	92.7	7.9	0.00	n.a.	n.a.	n.a.	42.1
PVC	94.8	4.8	0.4	41.4	5.3	5.83	0.04	0.03	47.7	22.8
Multi-material:										
Juice carton	86.0	6.1	7.9	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	24.4

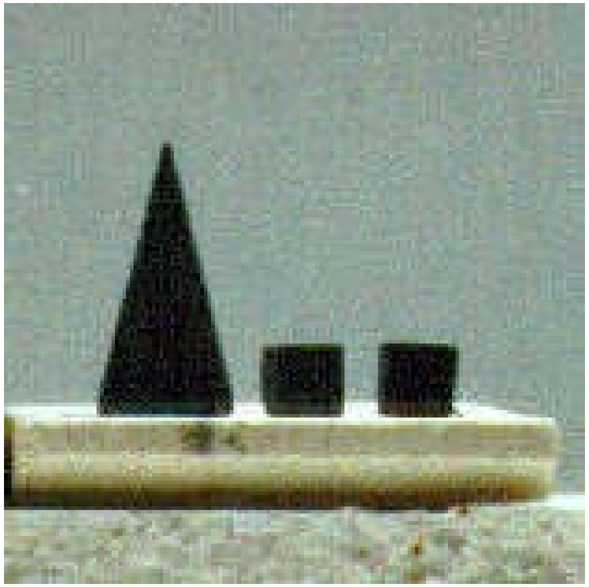
[a] Obtained by mass balance., [b] Ashed at 950°C., [c] Ashed at 575°C.

Coal

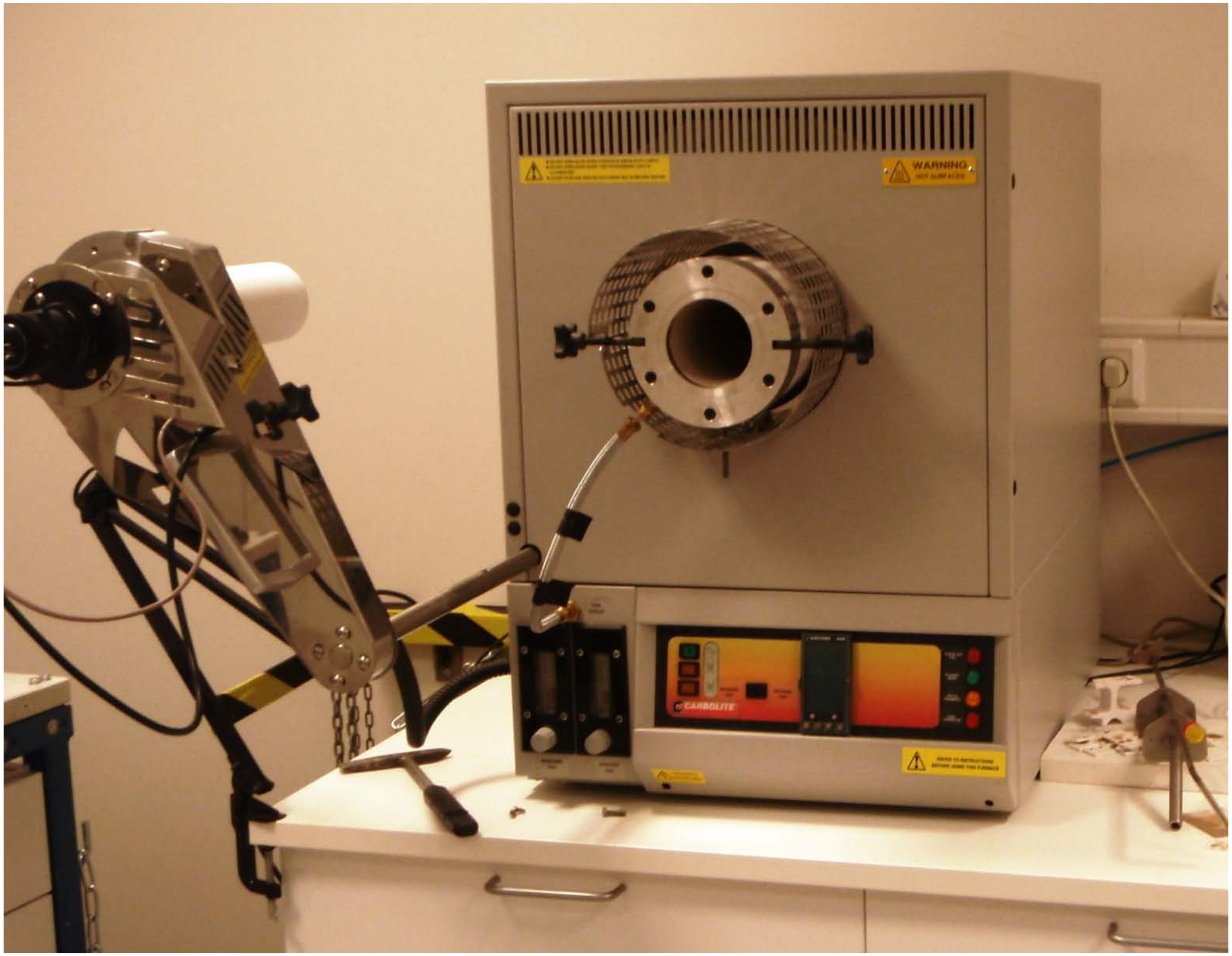
	Percent by weight									
	Proximate analysis				Ultimate analysis					
Fuel (state)	Carbon	Volatile matter	Moisture	Ash	C	H	N	O	S	Heating value (10^6 J kg^{-1})
Meta-anthracite (RI)	65.3	2.5	13.3	18.9	64.2	0.4	0.2	2.7	0.3	21.7
Anthracite (PA)	77.1	3.8	5.4	13.7	76.1	1.8	0.6	1.8	0.6	27.8
Semianthracite (PA)	78.9	8.4	3.0	9.7	80.2	3.3	1.1	2.0	0.7	31.3
Bituminous (PA)	70.0	20.5	3.3	6.2	80.7	4.5	1.1	2.4	1.8	33.3
High-volatile bituminous										
(PA)	58.3	30.3	2.6	9.1	76.6	4.9	1.6	3.9	1.3	31.7
(CO)	54.3	32.6	1.4	11.7	73.4	5.1	1.3	6.5	0.6	30.7
(KY)	45.3	37.7	7.5	9.5	66.9	4.8	1.4	6.4	3.5	28.1
(IL)	39.1	40.2	12.1	8.6	12.8	4.6	1.0	6.6	4.3	26.7
Subbituminous (CO)	45.9	30.5	19.6	4.0	58.8	3.8	1.3	12.2	0.3	23.6
Lignite (ND)	30.8	28.2	34.8	6.2	42.4	2.8	0.7	12.4	0.7	16.8
Brown coal (Australia)	15.3	17.7	66.3	0.7					0.1	8.6
Wood (Douglas fir, as received)	17.2	82.0	35.9	0.8	52.3	6.3	0.1	40.5	0	21.0

Ash melting

- The ash samples are prepared as pyramids or cubes
- The samples are heated in a reduced or oxidizing atmosphere in an oven
- The oven temperature is raised to a point below the expected deformation temperature
- Thereafter oven temperature is increased at a uniform heating rate of 3-7°C/min
- Through a control window at one end of the furnace tube the shape of the samples in the tube is shown and can be evaluated
- The temperatures at which the characteristic changes of shape occur are recorded

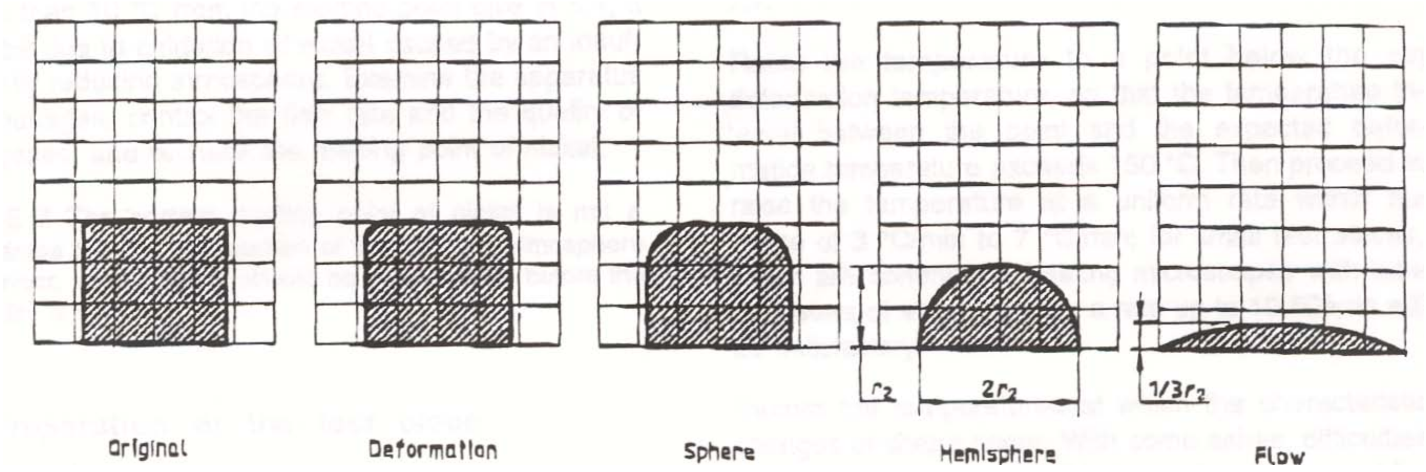


Ash melting



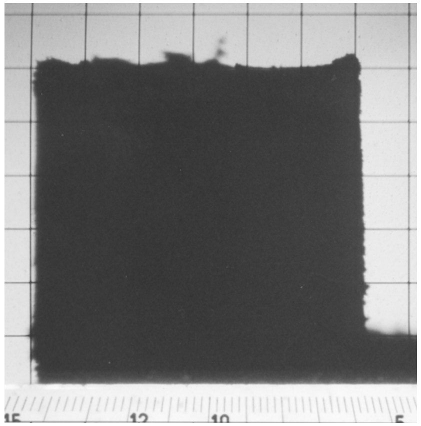
Ash melting

- Deformation temperature: The temperature at which the first signs of rounding due to melting, of the tip or edges occur.
- Sphere temperature: The temperature at which the edges of the test pieces become completely round with the height remaining unchanged.
- Hemisphere temperature: The temperature at which the test piece forms approximately a hemisphere i.e. when the height becomes equal to half the base diameter
- Flow temperature: The temperature at which the height is one third of the height of the test piece at the hemisphere temperature.

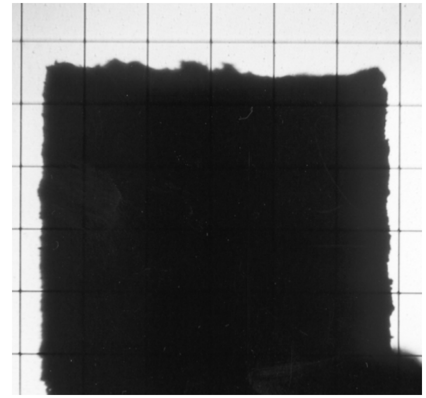


Ash melting

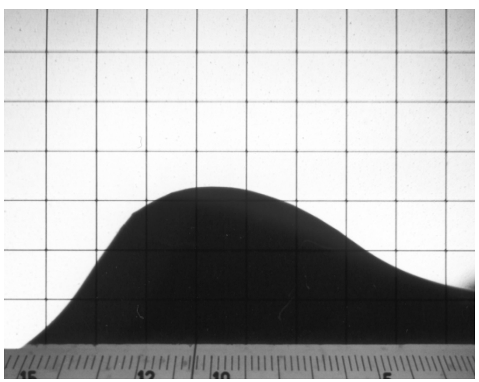
Example: ash from MSW



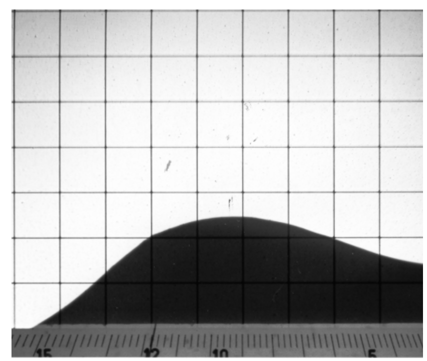
Original



Deformation temperature (sintering)
630-800°C



Hemisphere temperature
1050°C



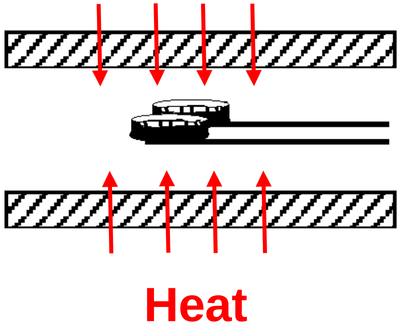
Flow temperature
1180°C

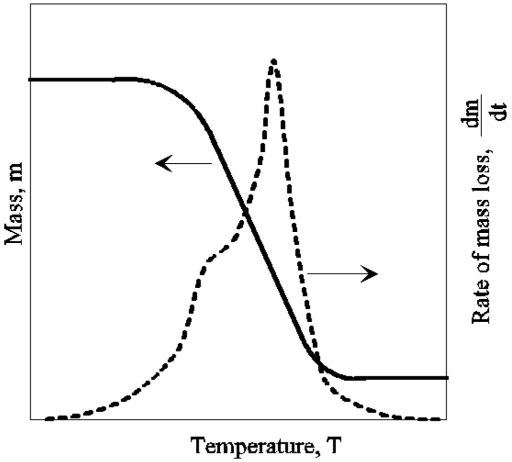
Thermal Gravimetric Analyses (TGA)

- The TGA apparatus yields continuous data of mass loss of a sample as a function of either temperature (dynamic) or time (isothermal) as the sample is heated at a programmed rate.

- The basic requirements for making a TG analyses is a high precision balance and a furnace.

- The results of a TGA run may be presented as:
  - mass vs. temperature or time curve (TG-curve)
  - mass loss vs. temperature or time curve (DTG-curve)



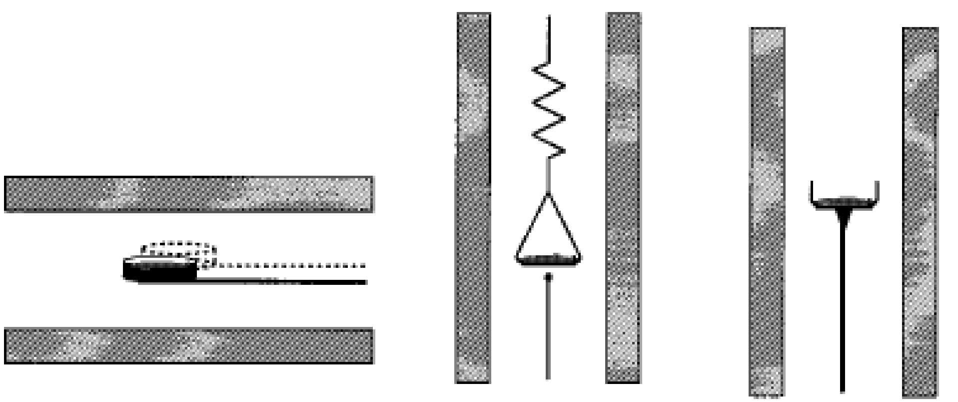


Thermal Gravimetric Analyses (TGA)

TA Instruments Simultaneous TGA/DSC

Application examples

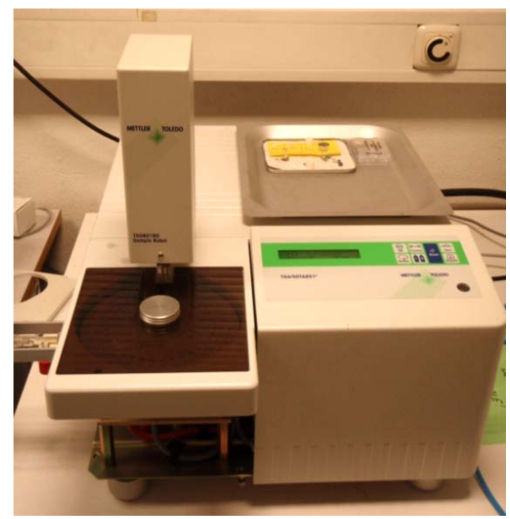
- Moisture and volatile content of materials
- Thermal stability of materials
- Decomposition kinetics of materials
- Atmosphere effects on materials



TA Instruments SDT 2960
Mettler Toledo TGA/SDTA851

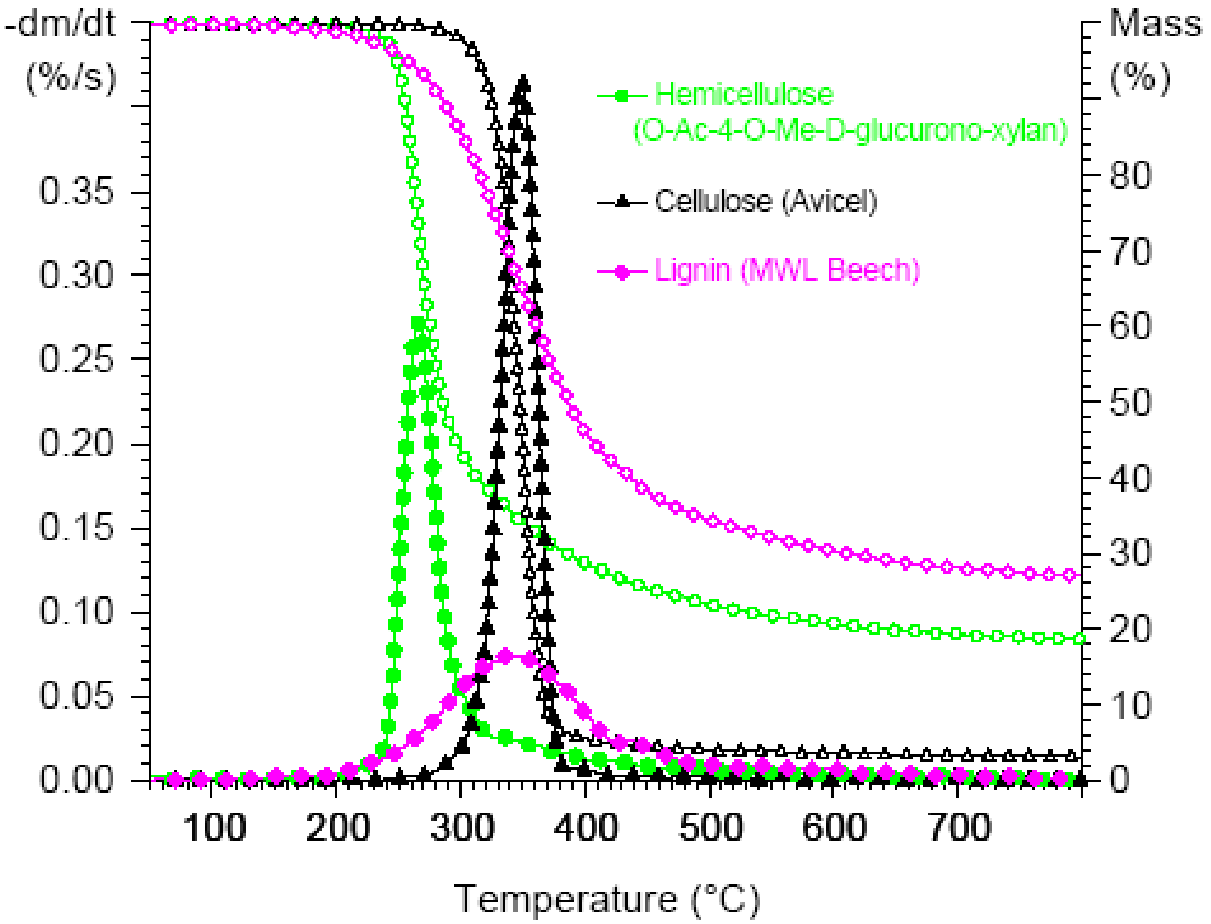
Perkin Elmer TGS 2
Perkin Elmer TGA 7

Netzsch STA 409C



Mettler Toledo

Pyrolysis of cellulose, hemicellulose and lignin



Pyrolysis of Wood

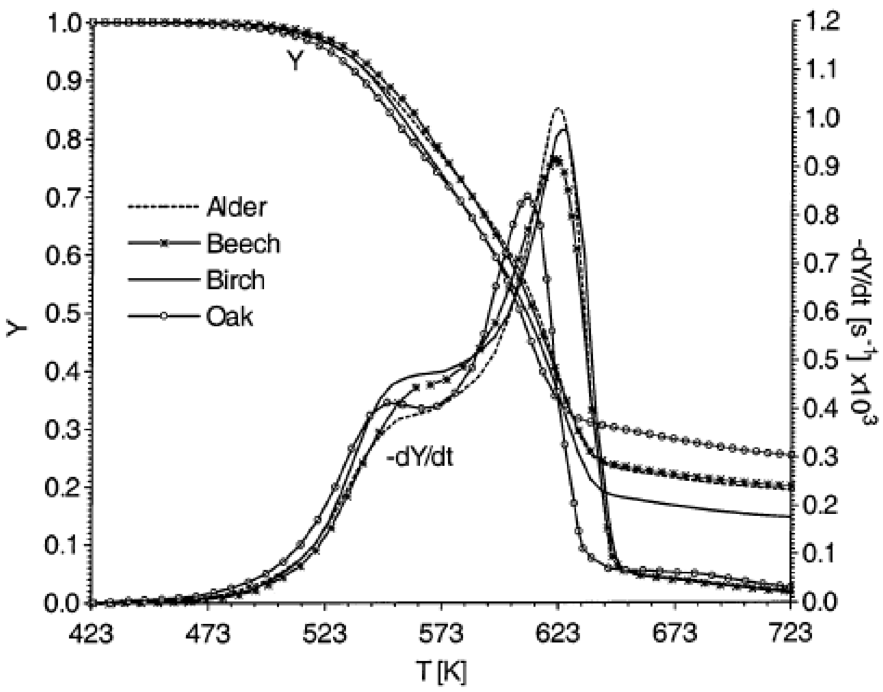


Figure 1. Mass fraction and time derivative of the mass fraction as functions of temperature for several hardwoods.

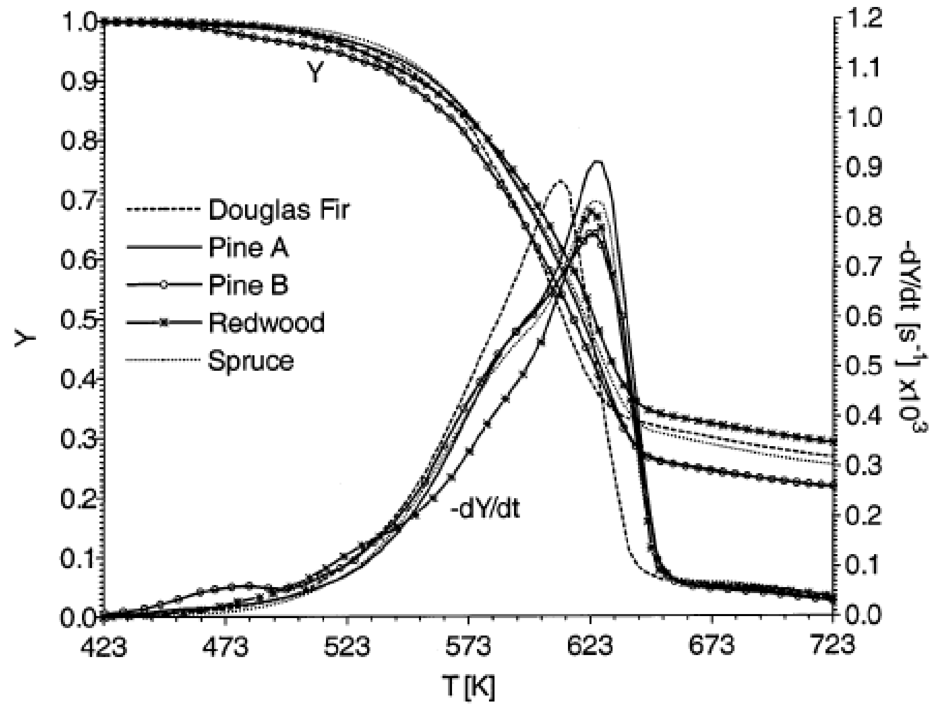


Figure 2. Mass fraction and time derivative of the mass fraction as functions of temperature for several softwoods.

Ind. Eng. Chem. Res. 2002, *41*, 4201−4208 4201

Thermogravimetric Analysis and Devolatilization Kinetics of Wood

Morten Gunnar Grønli,[†] Gábor Várhegyi,[‡] and Colomba Di Blasi*[§]

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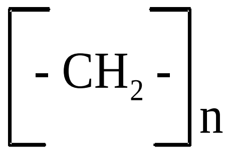
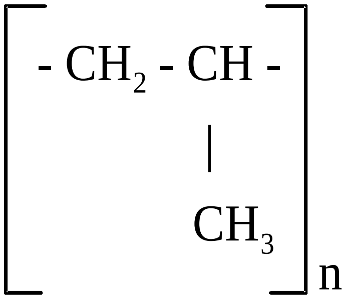
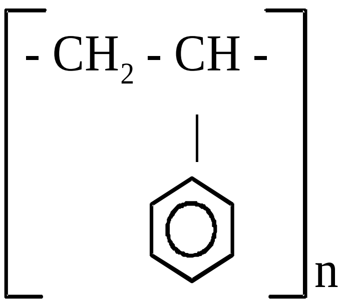
Chemical composition of plastics



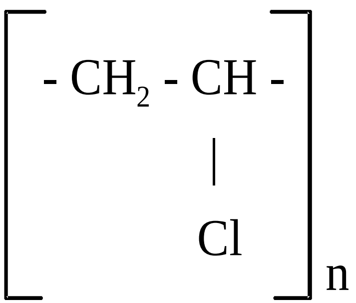
High Density Polyethylene (HDPE)
Low Density Polyethylene (LDPE)



Polypropylene (PP)



Polystyrene (PS)



Polyvinyl Chloride (PVC)

Pyrolysis of biomass and plastic

L. Sørum et al. / Fuel 80 (2001) 1217–1227 1221

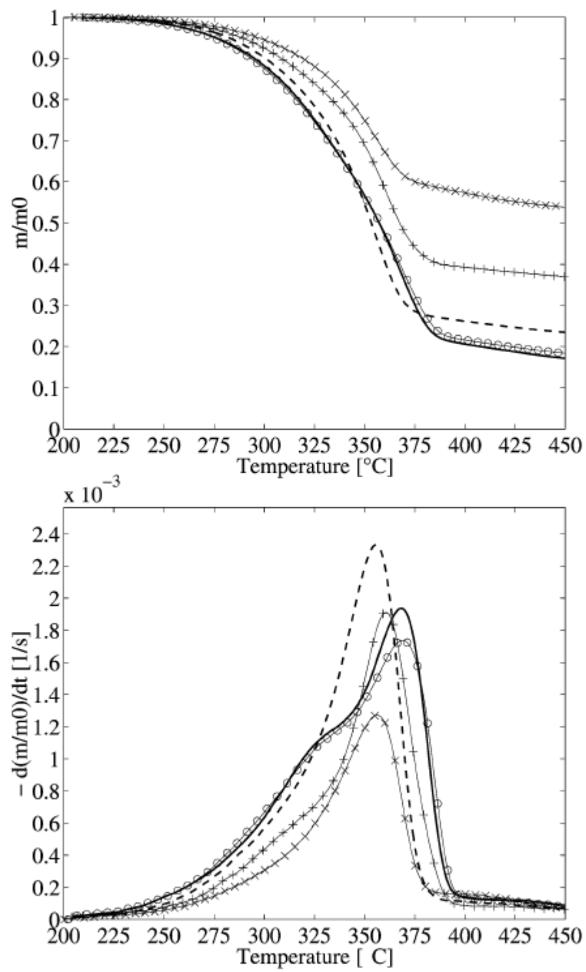


Fig. 1. TG and DTG curves of: spruce (——); newspaper (-○-○-○-); cardboard (- - - -); recycled paper (+ + + +); and glossy paper (-×-×-×-).

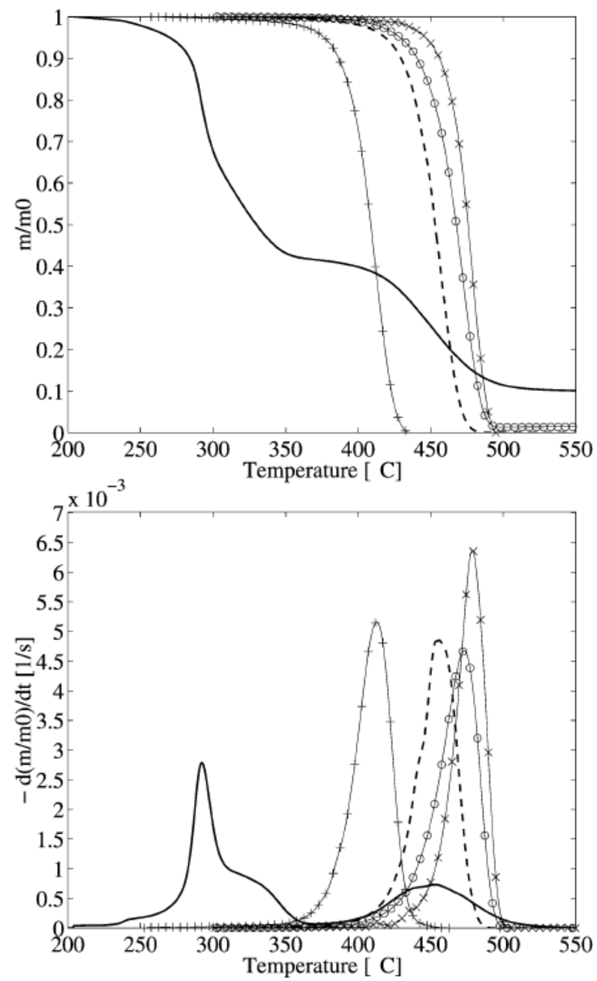
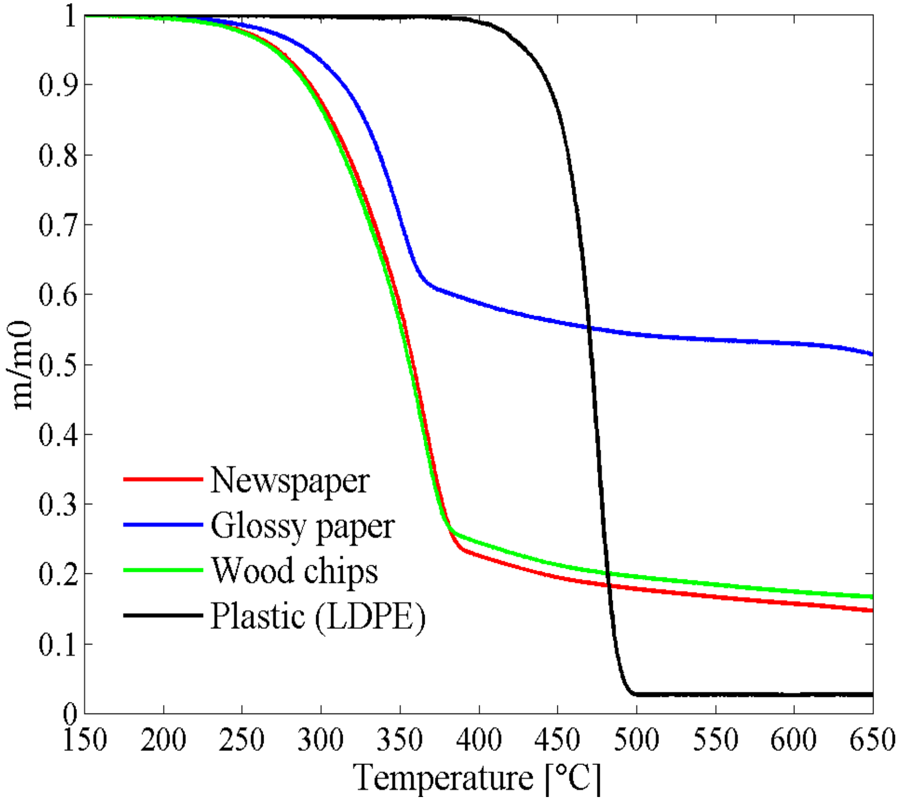
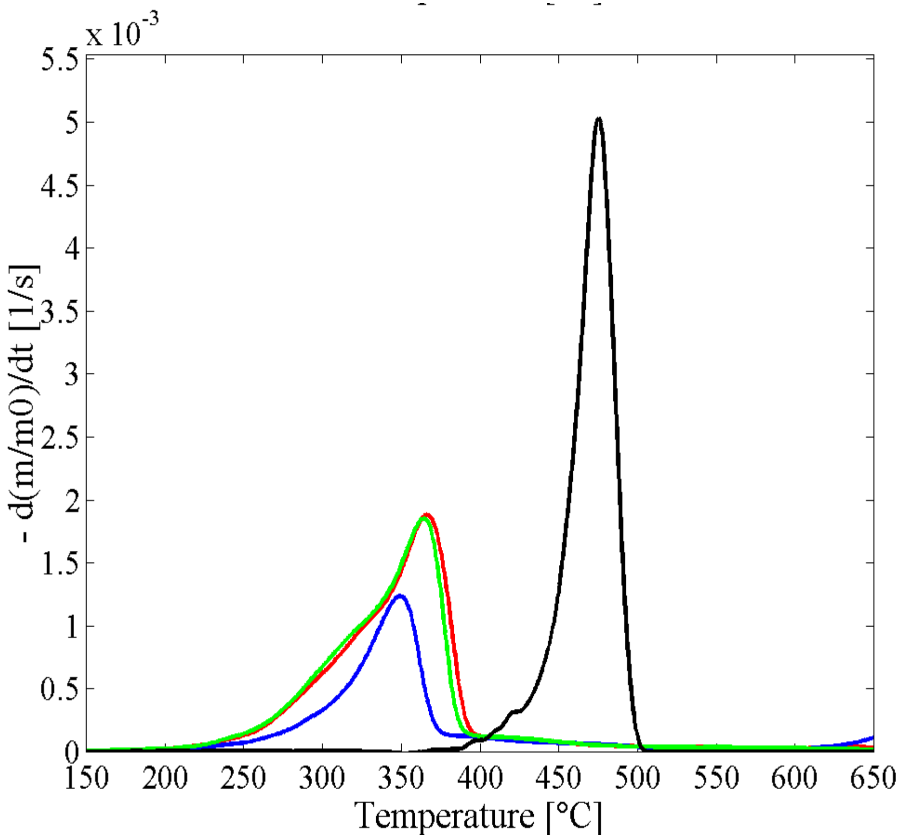


Fig. 2. TG and DTG curves of: HDPE (-×-×-×-); LDPE (-○-○-○-); PP (- - -); PS (+ + + +); and UPVC (——).

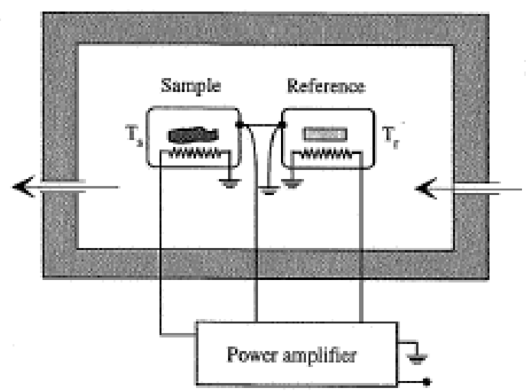
Pyrolysis of MSW

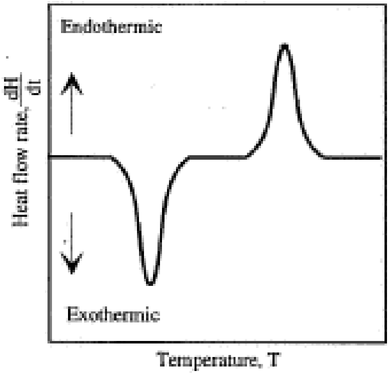




Differential Scanning Calorimeter

- (At least) two types of DSC instruments have been developed:
  - heat flux DSC (=DTA)
  - power compensation DSC
- In the power compensation DSC, the sample and reference material are placed in independent furnaces.
- When the temperature rises or falls in the sample material, power (energy) is applied to or removed from the calorimeter to compensate for the sample energy.
- The amount of power required to maintain the system equilibrium is directly proportional to the energy changes occurring in the sample.

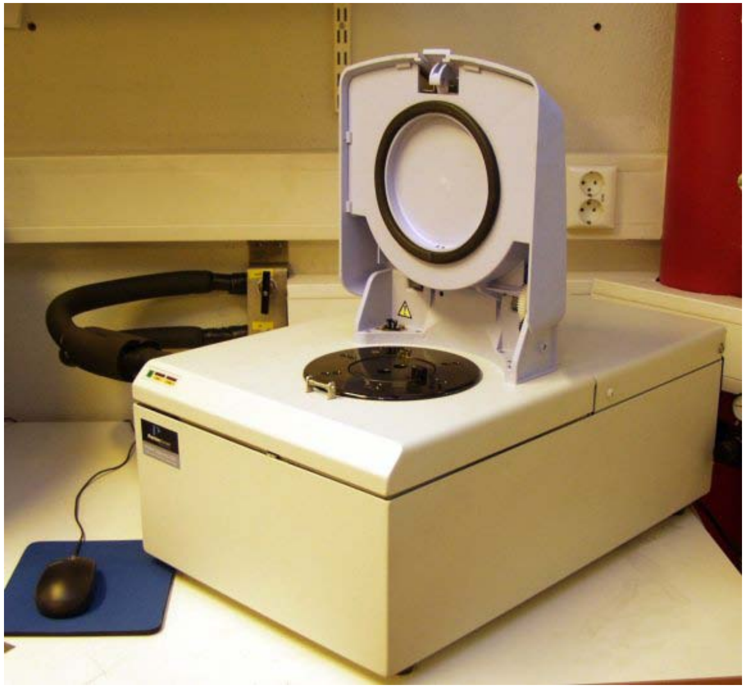




Differential Scanning Calorimeter

Application examples

- Heat of reaction
- Heat of fusion
- Glass transition
- Specific heat capacity



Perkin Elmer Pyris Diamon DSC