Automotive Fuels from Flash-pyrolysis of Biomass Bio-oils

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International Conference on Bioenergy and Liquid Biofuel Development and Utilization

7th LAMNET Project Workshop, Beijing, China 20-23 April 2004

EU Contract AIR1-CT92-0216

Cooperation Sardinia-Corse

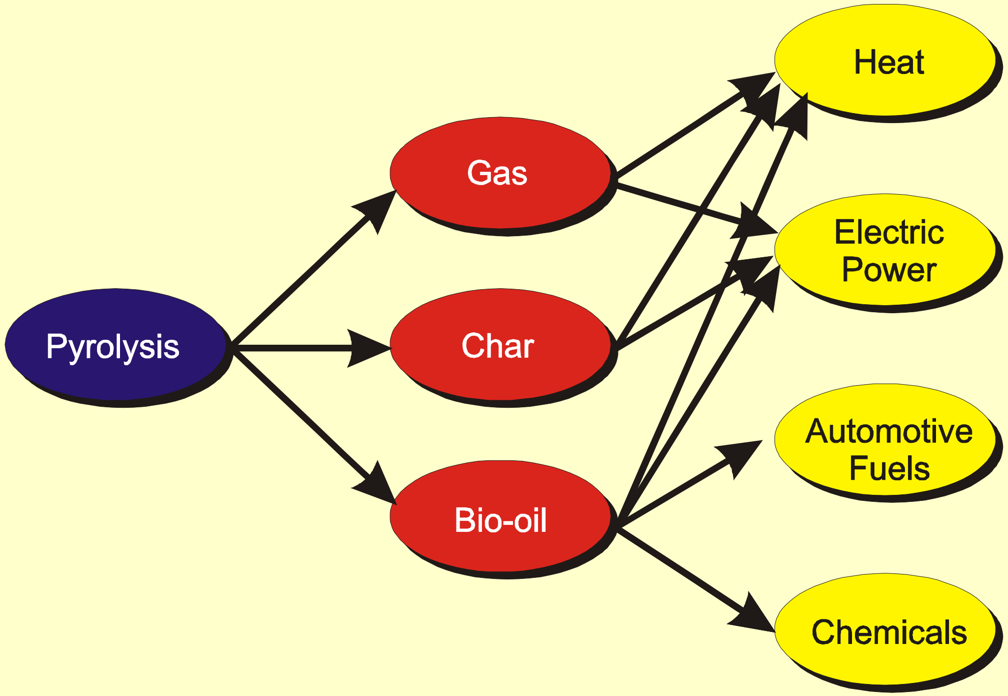
Project INTERREG II

Cooperation Sardinia-Corse-Tuscany

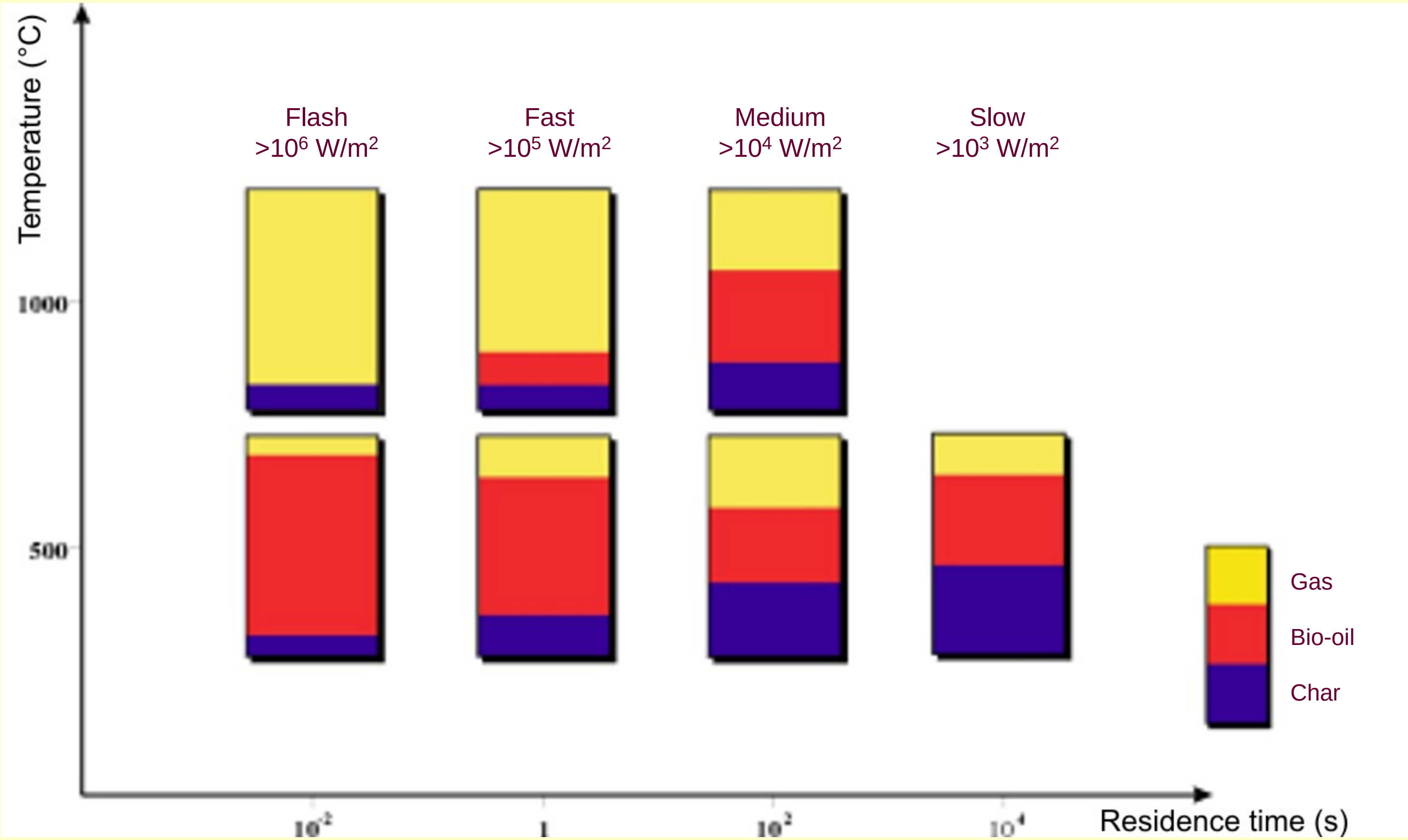
Project INTERREG III

Pyrolysis process

ENEL flash-pyrolysis demonstrative plant



Pyrolysis products distribution



Bio-oil quality

- High water content
- High acidity
- High viscosity
- Low heating value
- Instability versus temperature and storage time

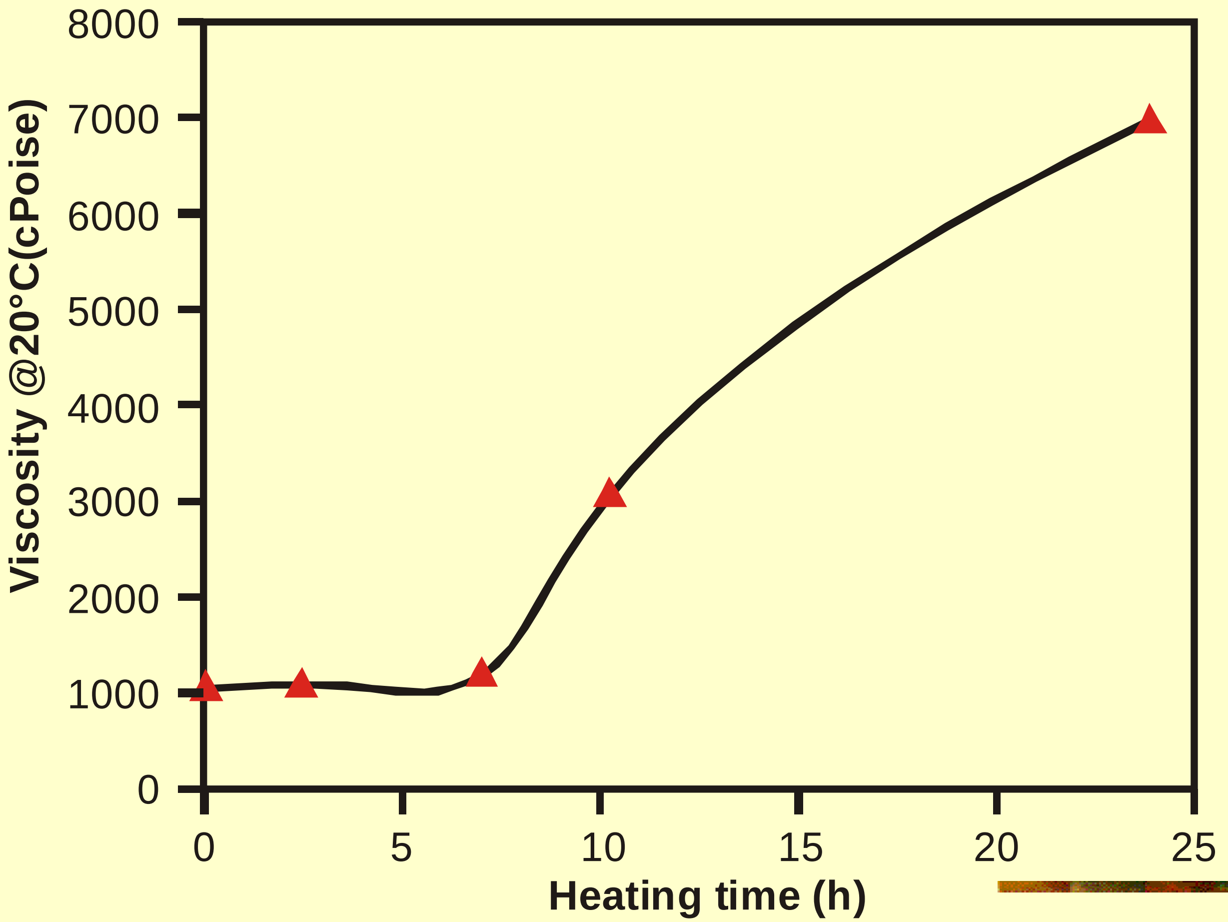
Typical characteristics of flash-pyrolysis bio-oil

pH		**2 - 3**
Density (at 15°C)	$g \cdot cm^{-3}$	**1 - 2**
Viscosity (at 25°C)	mPa·s	**65 - 70**
Ash	%wt	**0.15 – 0.20**
Moisture	%wt	**20 - 30**
HHV	MJ/kg	**15 - 19**
Flash point	°C	**52**
Pour point	°C	**-30**
Acetone insolubles	%wt	**0.5 – 3.8**
Elemental analysis (m.f.)		
C	%wt	**56 - 60**
H	%wt	**5.4 – 5.7**
N	%wt	**0.15 – 0.20**
O	%wt	**35 - 50**

Functional groups in flash-pyrolysis bio-oil

		Equivalents/kg bio-oil				
	Pyrolysis temp.	Carboxylic	Carbonylic	Hydroxylic	Phenolic	Methoxylic
Maple	480°C	2.1	5.7	0.92	2.8	2.1
Straw	500°C	1.4	5.3	1.40	3.0	1.1
Willow	450°C	2.1	6.2	0.77	2.8	1.6
Peat	520°C	1.2	3.0	1.30	1.8	0.7

Bio-oil viscosity vs heating time (at 100°C)



Bio-oil use in endothermic engines

- Limitations
  - Injection system corrosion
  - Ignition problems and low combustion speed
  - Deposit formation in the injection system and the combustion chamber

- Solutions
  - Low speed engines and pilot injection
  - Dual fuel engines (diesel fuel/bio-oil)
  - Bio-oil improvement

Bio-oil upgrading processes

Hydrotreating

$nC_2H_3O + 1.5n\ H_2 \longrightarrow (CH_2)_{2n} + nH_2O$

Advantages

- Uses existing technology in oil refining
- High catalyst stability
- Production of aliphatic hydrocarbons

Disadvantages

- High cost of hydrogen

Zeolite cracking

$2nC_2H_3O \longrightarrow (CH_2)_{3n} + nCO_2$

Advantages

- Hydrogen is not required

Disadvantages

- High coke production, with loss of catalytic activity
- Low hydrocarbon yields
- Production of aromatic and olefinic hydrocarbons

Hydrotreating process

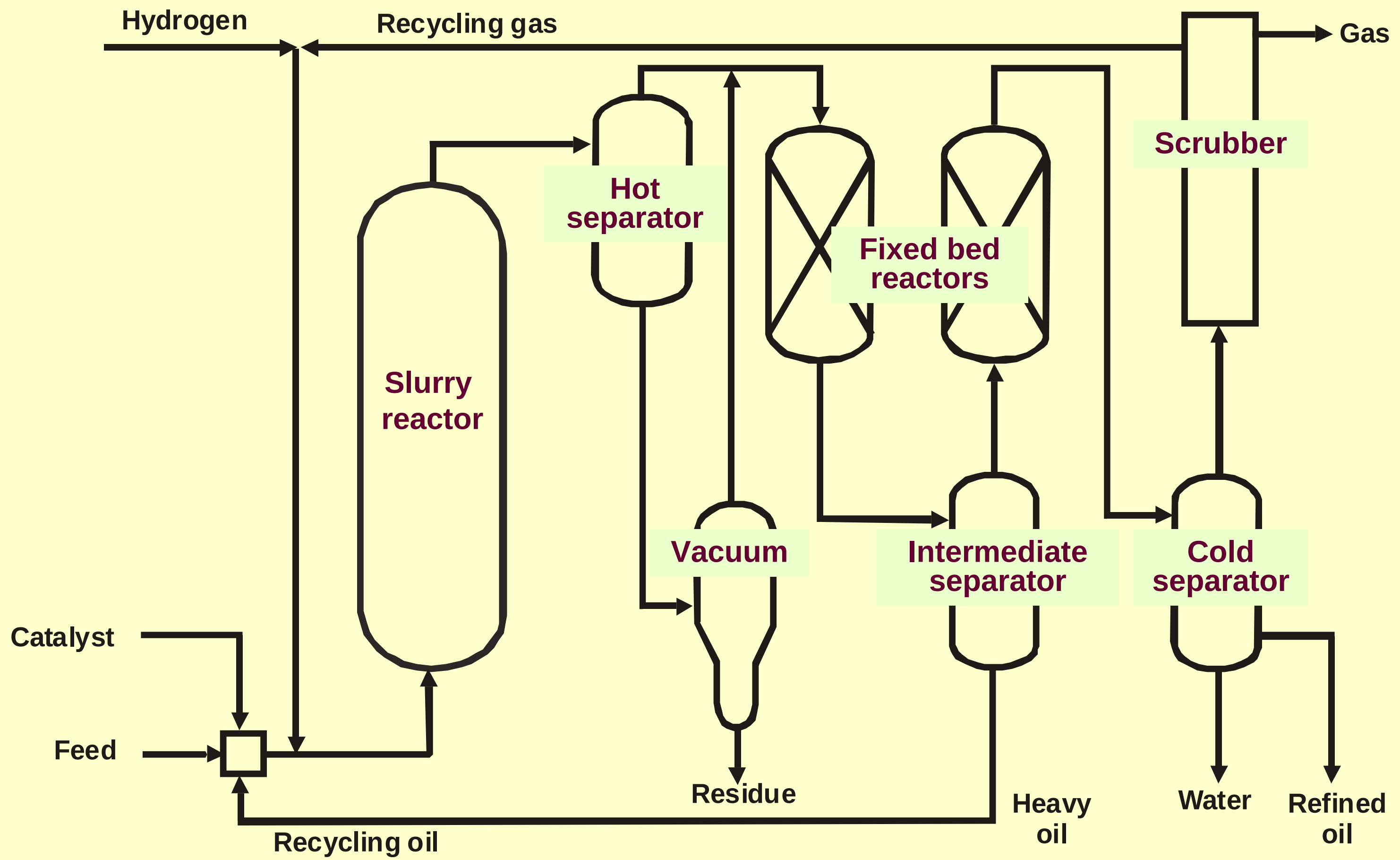
- Depolymerisation into small molecules
- Thermal decomposition into new molecular rearrangements
- Hydrogenolysis
- Hydrogenation of functional groups with oxygen and other heteroatoms elimination

Methodology

- Bench-scale fixed bed two stage process
  University of Sassari – Sassari (I)
- 10 kg/h pilot plant three stage IGOR technology process
  DMT - Gesellschaft für Forschung und Prüfung mbH – Essen (D)

1200 kg of bio-oil were hydrogenated by a continuous trouble free run

Hydrotreating pilot plant

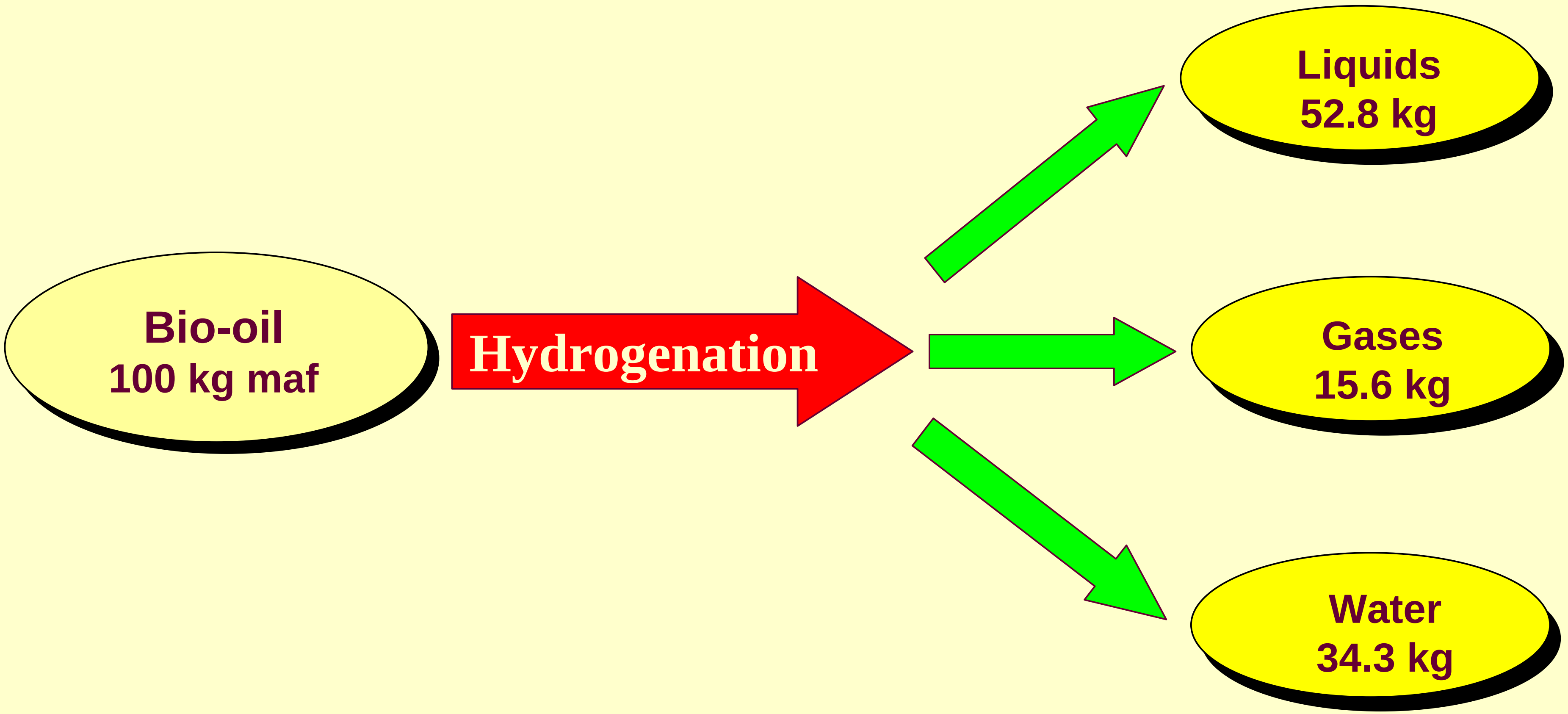


Source DMT

Pilot Plant operating conditions

❑ Bio-oil feed rate	11 kg/h
❑ Reactor volume	11 dm^3
❑ Specific oil feed rate	1 kg/dm^3 h
❑ Total pressure	30.0 MPa
❑ Reaction temperature	380°C
❑ Catalyst	Sulphurised NiMo (2.7% Ni, 13.3% Mo, γ-Al_2O_3)

Bio-oil hydrogenation yields



Analysis of bio-crude and hydrogenated oil

		Bio-crude	Low boiling syncrude
Density (at 20°C)	g/cm^3	**1.258**	**0.801**
Viscosity (at 20°C)	$mm^2 \cdot s^{-1}$	**857.8**	**1.35**
Pour point	°C		**<-35**
Flash point	°C		**<6**
Net calorific value (LHV)	MJ/kg	**19.8**	**43.7**
Coke residue	%wt		**0**
Ash	%wt		**0**
Water	%wt		**<0.05**
Boiling analysis			
I.B.P.	°C		**35**
50%	°C		**263**
90%	°C		**349**
F.B.P.	°C		**396**
Ultimate analysys			
C	%wt	**46.0**	**87.3**
H	%wt	**6.9**	**12.7**
O	%wt	**42.0**	**<<0.1**
N	mg/kg	**352**	**2**
S	mg/kg	**57**	**32**

Source DMT

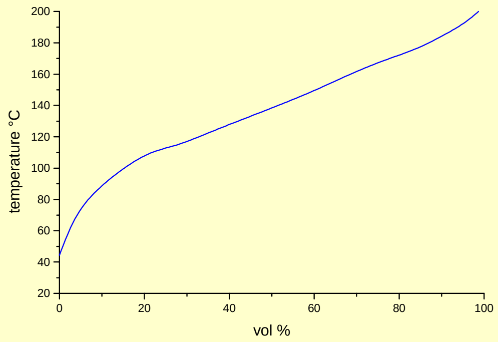
GC/MS characterisation of the hydrogenation process product

Peak N°	Retention time	Compound	Confidence coefficient	Conc (%wt)
1.	2.945	butane	90	0.14494
2.	3.203	2-methyl butane	90	0.55902
3.	3.438	pentane	90	3.53372
4.	4.358	cyclopentane	80	2.58248
5.	4.442	3-methylpentane	72	0.84159
6.	5.144	hexane	94	4.77522
7.	5.906	methylcyclopentane	72	4.56962
8.	7.039	cyclohexane	95	5.20708
9.	7.685	3-methyl hexane	93	0.62373
10.	7.973	1,3-dimethylcyclopentane	83	0.42351
11.	8.215	1,2-dimethylcyclopentane	90	0.39383
12.	8.802	heptane	97	1.42366
13.	9.890	methylcyclohexane	97	6.61314
14.	10.466	ethylcyclopentane	97	1.52265
15.	10.940	2-methylheptane	70	0.07283
16.	11.810	toluene	93	0.31971
17.	13.194	1,3-dimethylciclohexane	94	0.75092
18.	13.914	1-ethyl-3-methylcyclopentane	91	0.46813
19.	14.145	1-ethyl-2-methylcyclopentane	76	0.43856
20.	14.918	octane	93	0.99624
21.	14.993	1,3-dimethyl cyclohexane	96	0.53966
22.	16.654	1,2-dimethyl cyclohexane	94	0.33567
23.	17.140	ethylcyclohexane	95	5.03212
24.	18.450	ethylbenzene	86	0.28786
25.	19.182	xylenes	64	0.12160
26.	19.495	octahydropentalene	90	0.24589
27.	21.330	ethyl-methyl cyclohexane	87	1.61928
28.	22.721	nonane	93	0.64493
29.	22.945	methyl-ethylcyclohexane	64	0.67666
30.	24.999	propylcyclohexane	97	6.16768
31.	26.007	propylbenzene	90	0.53981
32.	26.688	hexahydroindan	91	0.47756
33.	27.925	etyl-methylbenzene	89	0.09129
34.	28.530	1- methyl-3-propylcyclohexane	90	0.07470
35.	29.416	1- methyl-2- propylcyclohexane	91	2.03729
36.	29.655	butylcyclohexane	90	0.72455
37.	31.891	methyl isopropylbenzene	94	0.21894
38.	32.477	indan	93	0.30370
39.	33.450	butylcyclohexane	90	0.82398
40.	33.790	methylhexahydroindan	95	0.89843
41.	34.263	*sec*-butyl benzene	90	0.36052
42.	34.642	butylbenzene	93	0.15987
43.	34.972	1-methyl-3-methyletenylcyclohexane	90	0.28140
44.	35.058	decahydronaphthalene	96	0.53459
45.	35.258	1-menthene	88	0.28479
46.	35.442	methyl-propyl-benzene	90	0.09304
47.	35.924	5-methylhexahydroindan	92	0.24987
48.	39.773	2-methyldecahydronaphthalene	97	1.16116
49.	41.858	pentylcyclohexane	93	0.73430
50.	42.180	pentylcyclohexene	55	0.44153
51.	42.629	tetrahydronaphthalene	97	0.35546
52.	45.951	methyl-butyl-cyclohexane	35	0.68020
53.	47.192	2-methyltetrahydronaphthalene	95	0.25402
54.	48.525	4-ethylindan	80	0.20979
55.	49.929	hexylcyclohexane	95	0.40973
56.	50.148	cyclododecene	58	0.42538
57.	50.775	5-methyltetrahydronaphthalene	94	0.43994
58.	52.639	6-methyltetrahydronaphthalene	95	0.29128
59.	54.578	bicyclohexile	91	0.38142
60.	54.887	2,7-dimethyltetrahydronaphthalene	90	0.26302
61.	55.063	1,5 dimethyltetrahydronaphthalene	90	0.16956
62.	57.530	decylcyclohexane	78	0.23843
63.	58.413	5-ethyltetrahydronaphthalene	64	0.28803
64.	59.908	6,7-dimethyltetrahydronaphthalene	98	0.09586
65.	61.640	1,4-dimethyltetrahydronaphthalene	89	0.07189
66.	66.986	tetradecahydroanthracene	76	0.16351
67.	67.859	1,2-dicyclohexyletane	90	0.50278
68.	68.275	1-phenil,2cyclohexiletane	90	0.00831
69.	74.670	1,3-dicyclohexilpropane	94	0.15502
70.	80.431	C17-paraffinic	96	0.14316
71.	86.068	C18-paraffinic	98	0.38444
72.	87.332	1,5-dicyclohexyilpentane	94	0.12866
73.	105.988	C22-paraffinic	98	0.02039
74.	119.281	C25-paraffinic	96	0.10263

Hydrogenated bio-oil composition

Raw hydrogenated oil
B.P. 35-396 °C

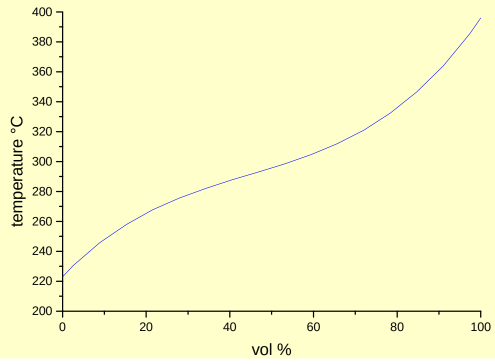
Light fraction
<210 °C
53.1%



Gasoline-like

Heavy fraction
>210 °C
46.9%

Gas oil-like



Industrial characterisation of light fraction

			Hydrogenated product light fraction	Commercial gasoline
Density (at 15°C)	ASTM D1298	g/cm^3	0.8038	0.725-0.77
Distillation	ASTM D86			
Initial Boiling Point		°C	34.4	> 30
10% evaporated		°C	**100.0**	< 70
20% evaporated		°C	108.0	
50% evaporated		°C	138.9	
90% evaporated		°C	**184.1**	< 180
Final Boiling Point		°C	199.6	< 215
Copper corrosion (3h at 50°C)	ASTM D130		absent	< 1
Vapour pressure (at 100°F)	ASTM D323	kg/cm^2	**0.108**	0.4 - 0.7
Gum test	ASTM D381	$mg/100cm^3$	< 3	< 8
Oxidation stability	ASTM D525	min	> 420	> 420
Clear octane number (Research)	ASTM D908		**53**	> 83
Neutralization number	ASTM D974	mg KOH/g	absent	< 0.04
Bromine number	ASTM D1159	gBr/100g	7.03	
Flash point	ASTM D93	°C	10	< 21

PONA analysis of light fraction

CLASS	Concentration (% wt.)	
	Hydrogenated product light fraction	Commercial gasoline *
***linear*-paraffins**	13.45	50 – 62
***iso*-paraffins**	11.88	
olefines	1.12	< 10
naphthenes	57.30	- - -
aromatics	16.25	< 40

(Specification of the CE 98/70 directive)*

Characteristics of the heavy fraction

			Hydrogenated product Heavy fraction	Commercial diesel fuel	Industrial gas oil
Density (at 15°C)	ASTM D1298	g/cm^3	0.9024	< 0.84	
Distillation	ASTM D158				
Initial Boiling Point		°C	224	> 170	
Recovered at 250°C		% vol.	11.5	< 65	
recovered at 300°C		% vol.	**53.8**	> 60 e < 80	> 50
recovered at 350°C		% vol.	**86.5**	> 87	
Final Boiling Point		°C	396	< 500	< 500
Colour	ASTM D1500		2.5	< 2	< 2
Flash point	ASTM D93	°C	102	> 55	> 55
Sulphur	ASTM D129	% wt.	0.025	< 0.03	< 0.07
Corrosion number	ASTM D130		absent	absent	absent
Cloud point	ASTM D97	°C	non detectable		< +50
Neutralisation No.	ASTM D974	mg KOH/g	0.27	< 2	
Oxidation stability	ASTM D525	min	> 420		
Cetane number	ASTM D976		**38.5**	> 47	> 30

Estimated costs ($/TOE)

❑ Pyrolysis bio-oil	423	*
❑ Pyrolysis bio-oil + hydrogenation + refining	820	* #
❑ Diesel fuel	390	§
❑ Biodiesel	787	§

* European price (PyNE Sept. 2003)

Plant 75.000 t/y (AIR-CT-92-0216 contract, updated)

§ Italian price 2003

Conclusions

- Hydrotreating of bio-oils obtained by flash-pyrolysis of biomass produces a raw, completely deoxygenated oil.
- The raw oil consist of a mixture of an industrial gas oil and a product which can be directly processed by normal refineries for automotive fuels.
- The production cost is rather higher than for fossil fuels but comparable to the cost of biodiesel produced in a plant of the same capacity (75,000 t/y).
- On the basis of a dry biomass yield of 20 t/ha, the yield of bio-naptha is about 5 t/ha; the yield of biodiesel is 1.5 – 2.5 t/ha.
- These results have to be confirmed in a demonstration plant.

Acknowledgements

- Dr. Gianfranco Scano
- Stefano Mascia, PhD