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DOSSIER Edited by/Sous la direction de : **A. Daudin et A. Quignard**

## PART 1

### Second and Third Generation Biofuels: Towards Sustainability and Competitiveness

#### Deuxième et troisième génération de biocarburants : développement durable et compétitivité

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- 621 > Editorial
- 633 > *Biomass Assessment: A Question of Method and Expertise*  
Évaluation de la ressource biomasse : une question de méthode et d'expertise  
A. Thivolle-Cazat, E. Le Net, F. Labalette and S. Marsac
- 651 > *Rational Formulation of Alternative Fuels using QSPR Methods: Application to Jet Fuels*  
Développement d'un outil d'aide à la formulation des carburants alternatifs utilisant des méthodes QSPR (*Quantitative Structure Property Relationship*): application aux carburéacteurs  
D.A. Saldana, B. Creton, P. Mouglin, N. Jeuland, B. Rousseau and L. Starck
- 663 > *Upgrading the Hemicellulosic Fraction of Biomass into Biofuel*  
Valorisation de la fraction hémicellulosique de la biomasse en biocarburants  
F. Ben Chaabane and R. Marchal
- 681 > *How Molecular Evolution Technologies can Provide Bespoke Industrial Enzymes: Application to Biofuels*  
Comment les technologies d'évolution moléculaire peuvent fournir des enzymes industrielles sur mesure : application aux biocarburants  
L. Fourage, J.-M. Sonet, F. Monot, G. Ravot and A. Margeot
- 693 > *The NILE Project – Advances in the Conversion of Lignocellulosic Materials into Ethanol*  
Le projet NILE et la conversion des matériaux lignocellulosiques en éthanol  
F. Monot, A. Margeot, B. Hahn-Hägerdal, J. Lindstedt and R. Slade
- 707 > *Synthesis Gas Purification*  
Purification des gaz de synthèse  
D. Chiche, C. Diverchy, A.-C. Lucquin, F. Porcheron and F. Defoort
- 725 > *Inorganic Species Behaviour in Thermochemical Processes for Energy Biomass Valorisation*  
Comportement des espèces inorganiques dans les procédés thermochimiques de valorisation énergétique de la biomasse  
K. Froment, J.-M. Seiler, F. Defoort and S. Ravel
- 741 > *Correspondence Between Structure and Reactivity During Hydrothermal Conversion of Lignocellulosic Macromolecules*  
Relation entre la structure et la réactivité en conversion hydrothermale des macromolécules de lignocellulosique  
J. Barbier, N. Charon, N. Dupassieux, A. Loppinet-Serani, L. Mahé, J. Ponthus, M. Courtiade, A. Ducrozet, A. Le Masle, A.-A. Quoineaue and F. Cansell
- 753 > *Thermochemical Conversion of Lignin for Fuels and Chemicals: A Review*  
Conversion thermochimique de la lignine en carburants et produits chimiques : une revue  
B. Joffres, D. Laurenti, N. Charon, A. Daudin, A. Quignard and C. Geantet
- 765 > *A Short Historical Review of Fast Pyrolysis of Biomass*  
Une brève revue historique de la pyrolyse rapide de la biomasse  
D. Radlein and A. Quignard

# A Short Historical Review of Fast Pyrolysis of Biomass

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**Résumé** — **Une brève revue historique de la pyrolyse rapide de la biomasse** — Dans cette revue nous nous proposons de dresser un rappel historique des progrès relatifs aux technologies de liquéfaction thermochimiques par pyrolyse rapide, encore appelée pyrolyse flash, de la biomasse pour produire ce que l'on appelle communément une "bio-huile". Nous insisterons sur ses applications comme combustible liquide pour la production de chaleur et d'électricité. Nous ferons ressortir quelques propriétés spécifiques aux bio-huiles qui peuvent créer des difficultés d'usage. Nous terminerons par un bref aperçu de quelques procédés permettant de valoriser la bio-huile en carburants liquides de plus forte valeur ajoutée.

**Abstract** — **A Short Historical Review of Fast Pyrolysis of Biomass** — In this short review, we survey the historical progress of fast pyrolysis technologies for thermochemical liquefaction of biomass to produce so-called "bio-oil". Our focus is on the potential applications of bio-oil as a liquid fuel for heat and power generation. We point out some of the inherent properties of bio-oil that create difficulties standing in the way of these applications. Finally, we take a brief look at some processes that aim to valorize bio-oil by conversion to higher value liquid fuel products.

## INTRODUCTION

In the transition to a sustainable energy future, biomass is naturally seen as potential source of carbon based fuels and chemicals. While many theoretical routes to accomplish the conversion can be envisaged, in the short run what is required are practical and demonstrated methods. Industrial scale thermochemical production of liquids, bio-oils, by fast or flash pyrolysis has been demonstrated, but nevertheless it has so far not been adopted in commercial practice.

In this short review, we shall attempt to summarise the modern history of the fast pyrolysis of biomass over the past thirty years or so. We emphasize that it is not intended to a exhaustive account, but is rather a personal perspective on the main threads in the evolution of what is now known as fast or flash pyrolysis. Thus “slow pyrolysis” techniques like those utilizing packed beds, vacuum pyrolysis nor hydrothermal approaches to biomass liquefaction will not be discussed.

## 1 FAST OR FLASH PYROLYSIS

Pyrolysis of biomass refers to its thermal decomposition by heating in an inert atmosphere. Under these conditions, the biomass decomposes into solids (char), water, gases composed of carbon oxides, hydrogen and hydrocarbons as well as myriad organic molecules. The gaseous product stream therefore contains both condensable and non-condensable vapours and aerosols. Bio-oil is the liquid product condensed from the gaseous outlet stream.

The relative amounts of the various products depends on various factors important among which is the heating rate. Generally, fast or flash pyrolysis refers to heating rates greater than about  $\sim 1000^\circ\text{C/s}$ .

The heat required for fast pyrolysis, including both the sensible heat required to raise the temperature of the biomass to the pyrolysis temperature as well the heat of the pyrolysis reactions has been found to be of the order of  $\sim 1\text{--}2$  MJ/kg of biomass containing  $\sim 10\%$  moisture [1].

Woody biomass is composed mainly of cellulosic and lignin polymers together with various extractives along with a small amount of inorganic matter. The products of its thermal decomposition of biomass are determined principally by the relative proportions of the various components together with the decomposition temperature. For example, it is well known that the three principal components of woody biomass, cellulose, hemicelluloses and lignin, show substantially different weight-loss profiles (*i.e.* different temperatures of

maximum rate of weight loss) at the same heating rate on thermogravimetric analysis (TGA).

Pyrolysis generally proceeds by an array of serial and parallel reactions with a wide range of activation energies. The same is also true for minor components like extractives, bark and proteins. Consequently, the spectrum of products is critically dependent on the biomass heating rate and final temperature (it should be borne in mind that the temperature of the decomposing biomass is not necessarily coincident with that of the pyrolysis vessel).

Piskorz *et al.* [2], showed that the predominant functional groups present in bio-oil were carbonyl, phenolic and carboxylic. These groups are distributed between those products originating from the cellulosic components of the biomass and those arising from lignin. The former are mostly soluble in water while the latter are mostly insoluble. Addition of sufficient water to a single-phase bio-oil generally results in separation of a “heavy tar” fraction that was identified as originating largely from the lignin component of biomass [3], also called pyrolytic lignin.

Broido and Kilzer [4] first called attention to the great sensitivity of the pyrolytic decomposition pathways of cellulose to very small amounts of inorganic impurities ( $< 0.1\%$ ) which markedly alter the degradation characteristics of cellulose. In particular, they promote the destruction of anhydrosugars to smaller fragments with accompanying formation of char. Furthermore some inorganic constituents, particularly alkaline salts, can greatly accelerate char formation. For example, it has been found that even a few ppm of sodium salts can increase the char yield from the pyrolysis of pure crystalline cellulose by a factor of greater than 10 [5].

Later, it was shown that de-mineralization of the biomass, especially the removal of alkali cations, can lead to very large increases in organic liquid yields, with enhanced formation of anhydrosugars [6]. However besides the added expense of demineralization by acid treatment, the viscosity of the sugary bio-oil is also much higher leading to operational difficulties in tar recovery.

## Kinetic Models

Since pyrolytic decomposition of biomass proceeds through innumerable chemical reactions, kinetics are usually modelled by simple lumped phenomenological schemes in which the biomass is ultimately decomposed to solids (char), condensable liquids (“bio-oil”) and permanent gases. Most usual schemes are based on the the so-called Shafideh-Broido model, [7], in which the biomass is first converted to an “active” state that

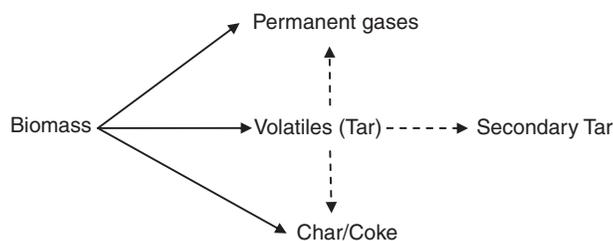


Figure 1

Thurner and Mann kinetic scheme for biomass pyrolysis.

subsequently decomposes into the final products through serial and parallel first order reactions. The most important pathways are a low temperature, low activation energy pathway producing mainly char and gas and a high temperature, high activation energy pathway producing mainly condensable vapours, gases and aerosols. *E.g.*, the modified Shafizadeh scheme illustrated in Figure 1 allows for secondary disproportionation of the primary tar to gases, secondary tar and char/coke and was used by Thurner and Mann, [8] and many subsequent authors. A recent review by Prakash and Karunanithi, [9], summarizes many of the published models.

In order to maximize liquid yields, the goal of fast pyrolysis, it is therefore important to heat the biomass rapidly to a suitably high temperature. However this is problematic since wood exhibits poor thermal conductivity ( $\sim 0.1 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ) so that rapid heating to a desired uniform temperature is extremely difficult and can only be approached in the limit of small particle sizes, typically about a few mm.

Low temperature reactions are dominated by release of low molecular gaseous products and cross-linking reactions that lead to char formation. At sufficiently high heating rates, the biomass can be brought to temperatures at which it initially liquefies to a high molecular weight viscous “melt” [10]. This melt continues to decompose to ultimately produce low molecular weight gases and vapours and aerosols. This melt is often treated as an intermediate in empirical kinetic modeling of biomass pyrolysis reactions where it is designated as “active” material (*Fig. 1*).

By combining a suitable kinetic model for a specific biomass feedstock with equations for heat transfer, predictions of yields of char, bio-oil and gases may be made for a particular reactor design. In a recent example Al-Haddad *et al.* [11], have carried out such a program for pyrolysis of fir sawdust pellets in a fluidized bed.

Many of the molecules in bio-oil are of very high molecular weight such that they cannot exist as vapour at the reaction temperature and instead, are present in

the gaseous phase as components of liquid aerosols. It was hypothesized by Radlein [12], Piskorz *et al.* [13], that these aerosols arise by direct mechanical action from liquefied biomass rather than by recombination reactions as previously thought. This has recently been confirmed by Teixeira *et al.* [14], who showed that the mechanism of their generation is by the collapse rather than by the ‘thermo-mechanical ejection’ (bursting of bubbles) as originally proposed. However Bayerbach and Meier, [15], provide evidence that recombination reactions, either in the gas phase during pyrolysis or during aging of condensed bio-oil, is at least partially responsible for some of the high molecular weight pyrolysis products.

It should be emphasized that the vapours and aerosols that are the immediate products of pyrolysis are prone to further decomposition and recombination reactions on prolonged exposure to a high temperature regime, ultimately decreasing bio-oil yield and increasing the amounts of gases and “intractable” tars. These secondary reactions place strong constraints on the design of reactors for production of bio-oil. Their kinetics have been studied by several authors, (*e.g.* Liden [24], *etc.*).

The heat requirement for pyrolysis is typically of the order of a few MJ/kg. Most of the heat requirement for pyrolysis is the sensible heat required to raise the biomass to the reaction temperature; the net heat of the pyrolysis reactions is usually small and may be endothermic or exothermic. This may be compared with the HHV (High Heating Value) of the bio-oil product which typically is around 18~20 MJ/kg with a water content of  $\sim 20\%$  for a biomass feed containing about 5 wt% of moisture. It must be borne in mind that increased water content of the biomass feed will increase the heat demand for pyrolysis and also increase the water content of the bio-oil, consequently reducing its heating value and decreasing overall efficiency. This has to be set against the cost of drying the biomass feed.

Slow pyrolysis in which long residence times at relatively low temperatures (less than about  $400^\circ\text{C}$ ) are employed, generally yields char and gas as the main products. As yet discussed, this approach is not discussed in this review. On the other hand, fast or flash pyrolysis typically employs final temperatures in the range of about  $450$  to about  $650^\circ\text{C}$  in which liquid yields can practically be maximized.

A study by Solantausta *et al.* [16] concluded that atmospheric flash pyrolysis of wood had the lowest product cost of the various approaches to liquefaction of biomass. Although performed more than twenty years ago, this assumption currently makes sense, mainly because it is a robust and reliable process as demonstrated in various pilot plants, demonstration units and on industrial type unit.

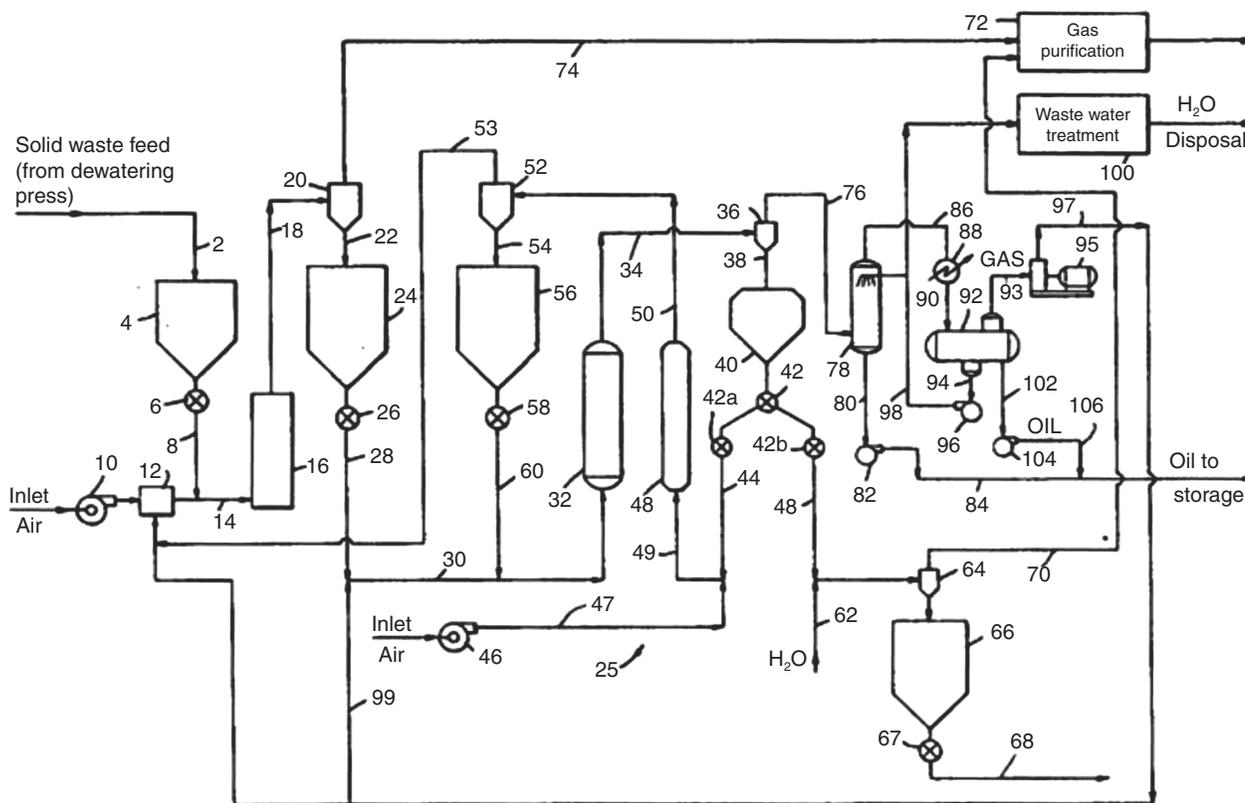


Figure 2

Illustration of the Garrett process [17].

## 2 DEVELOPMENT OF FAST PYROLYSIS TECHNOLOGIES

### 2.1 Garrett Process

Although the pyrolysis of coals has been studied for many decades, the pyrolysis of biomass to produce “bio-oil” for fuel purposes is of somewhat more recent vintage. A good point of departure is probably the 200 t/d RDF (Refuse Derived Fuel) pyrolysis plant built by the Occidental Research Corporation in San Diego, USA, in the 1970’s and illustrated in Figure 2. This plant was based on the process patented by Garrett and Mallan [17]. Although the feed was not strictly “pure biomass” since it might have included plastics and rubber for instance, nevertheless it did provide inspiration for the concept of fast pyrolysis of biomass.

The Garrett process is illustrated in Figure 2. In outline, shredded waste solids stored in a surge bin (24) are intimately intermixed with hot char, stored in the hot char hopper (56), and hot recycle gas (99). The entrained solids then pass through the pyrolysis reactor (32) under turbulent conditions with zone residence time

of under 10 seconds at a temperature of about 800°C. The char is removed by a cyclone (36) and the liquid product condensed in a quench tower (78). A tar was separated from an aqueous phase in a phase separator (92). A portion of the char product is combusted in a char heater (48) partly to provide process heat and partly to provide hot char for pyrolysis. Liquid yields could be as high as 40 mass% of the feed but char yields could also be equally high. The liquid was envisaged as a low-sulfur replacement fuel for No. 6 fuel oil.

However the project did not prove economically viable and the plant closed for lack of funding. We also now recognize that at these temperatures and residence times “pure biomass” would in fact produce mostly gas and a smaller amount of char.

### 2.2 Georgia Tech Entrained Bed Process

A subsequent significant and influential development was the *Georgia Tech* entrained flow pyrolysis process (Fig. 3) developed in the late 1970’s to the early 1980’s, Kovac *et al.* [18]. Here the biomass feed is crushed to

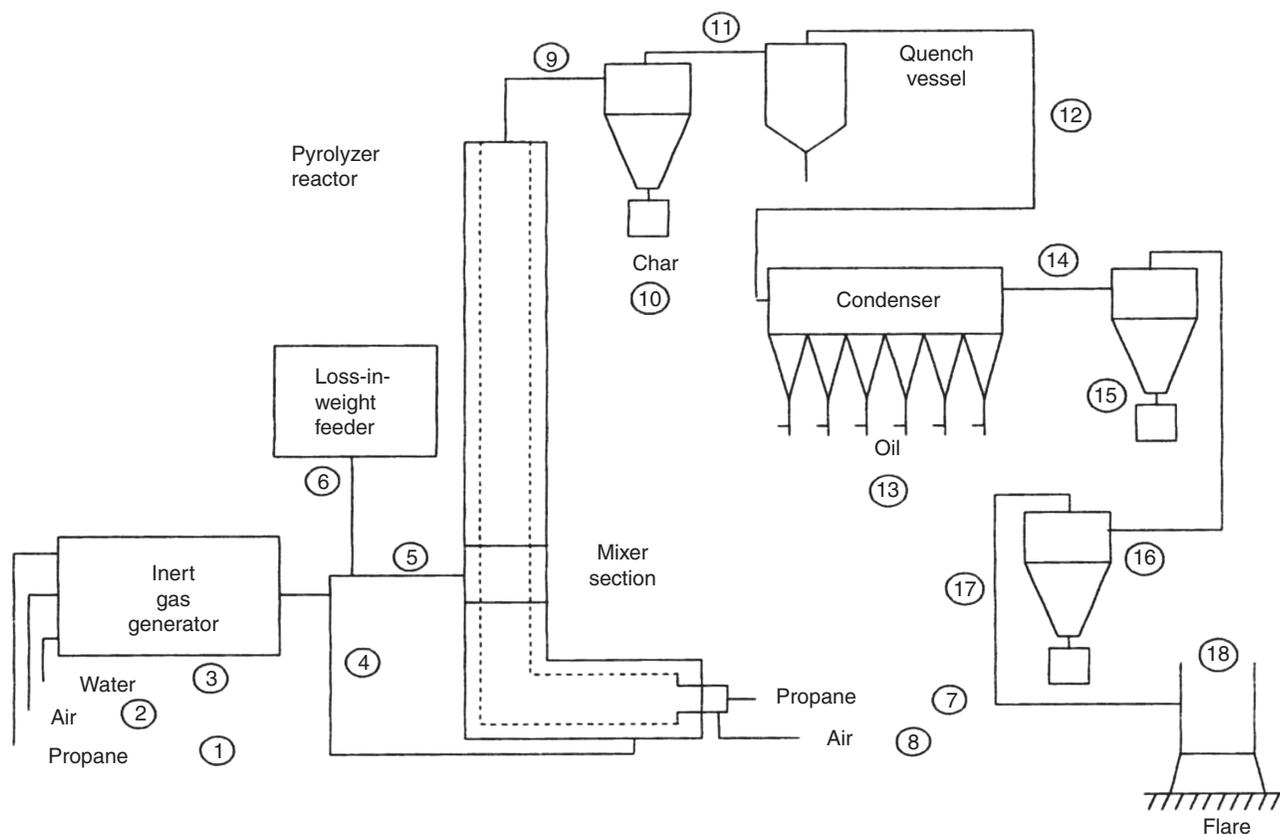


Figure 3

The Georgia Tech entrained flow pyrolysis system (taken from Kovac *et al.* [18]).

particles sizes around 1 mm and dried to about 10% moisture. The feed is pneumatically transported by an inert gas into a zone where it is entrained in a preheated inert gas stream and carried in up-flow to the reactor outlet.

Liquid yields up to about 50 mass% of the feed were obtained when the reactor outlet temperature was about 500°C, while char yields were in the range of about 20-30 mass%. Residence time is determined by the reactor height and the gas flow rates. Particle residence times were usually of the order of several seconds. Heat was supplied by gas convection from the inert product gas resulting from the combustion of propane in air which is mixed with the biomass feed entrained in an inert gas.

This concept has been further developed by *Egemin* in Belgium where a 200 kg/h pilot plant was built, [19].

A significant problem with entrained flow pyrolyzers is that a substantial fraction of the heat requirement for pyrolysis would be provided by the entraining gas which will have a low heat capacity while, as we discuss subsequently, high liquid yields of from biomass requires

a high heating rate of biomass particles to the desired reaction temperature.

A second problem is the fact that it has generally been found that fresh biomass char exerts a catalytic effect on cracking of bio-oil to produce more char and gas.

## 2.3 Fluidized Bed Pyrolysis Processes

On account of their excellent heat transfer characteristics, fluidized beds offer an efficient means to heat finely divided biomass rapidly to the desired pyrolysis temperature. Since fluidized beds represent a well-established technology it was inevitable that they would constitute the basis for those pyrolysis processes that have been demonstrated at the largest scales, several hundred tons/day, so far.

### 2.3.1 Waterloo Flash Pyrolysis Process (WFPP)

The next significant development was the work of Scott and his group at the *University of Waterloo*, Canada, in

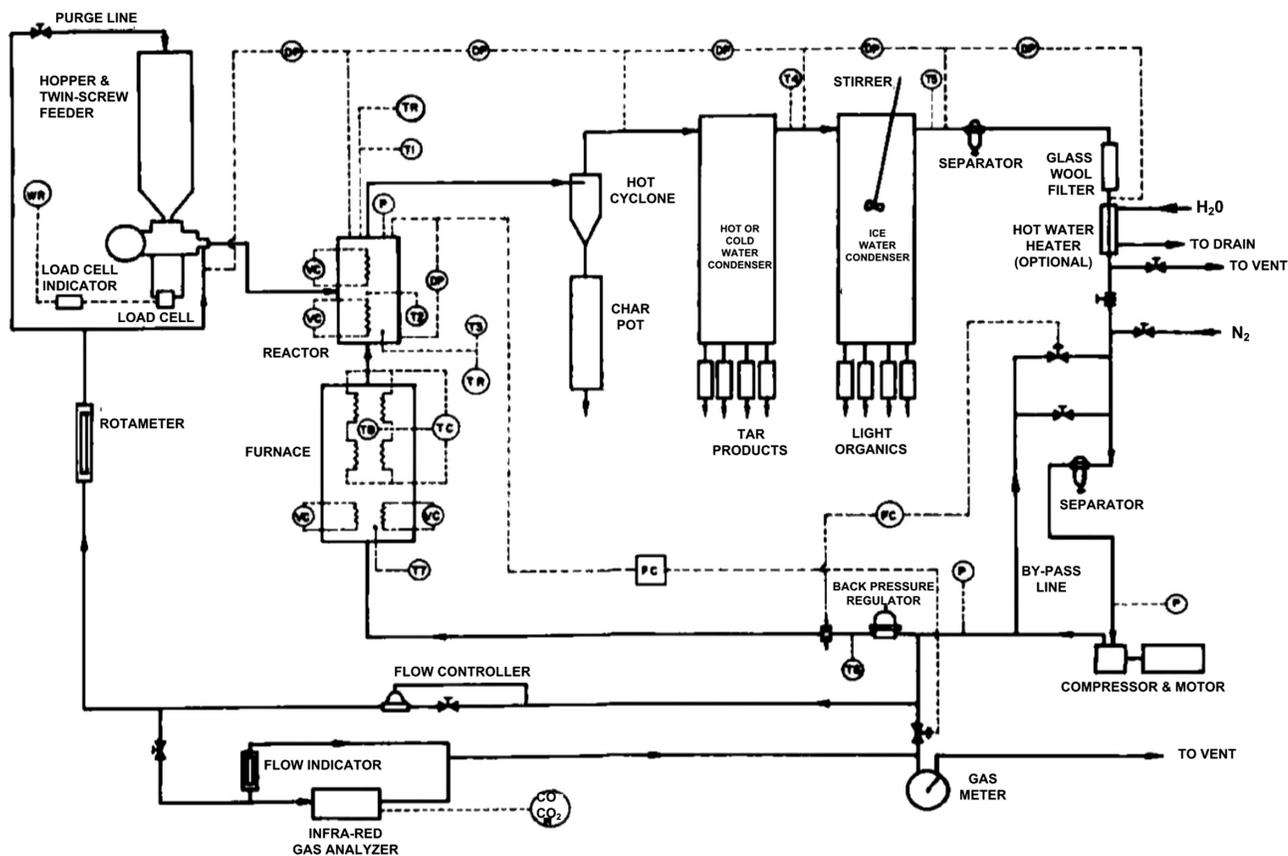


Figure 4  
Schematic of the Waterloo Fast Pyrolysis Process pilot plant.

the 1980's and 1990's that provided the inspiration for the development of several quasi-commercial scale pyrolysis systems.

They showed that very high yields of liquids could be obtained by pyrolysis of finely divided biomass in a bubbling fluidized bed in a bench-scale pyrolyzer [20]. They reported bio-oil yields as high as ~80% from very finely divided (~0.1 mm) clean Aspen Poplar wood and extremely short gas residence times (< 1 s). The process was scaled up to 3 kg/h pilot plant (Fig. 4) [21], with similar results (Tab. 1).

The pilot plant reactor was a sand bed fluidized and partially heated by recirculated and re-heated product gas. Finely ground biomass was injected into the bed pneumatically.

Subsequently it became apparent that with larger particle sizes and longer gas residence times, ~1 mm biomass particles and residence times of several seconds, bio-oil yields were only marginally lowered.

An implementation of the WFPP at *Union Fenosa* in Spain was the first demonstration fluidized bed, fast pyrolysis process. The 200 kg/day plant is more fully described in a PyNE newsletter [22].

### 2.3.2 RTI Process (Resource Transforms International)

In the WFPP, it was supposed that very short residence times (< 1 s) were required to obtain maximum bio-oil yields and hence required shallow fluidized beds and/or high fluidizing gas rates. However subsequent work at RTI established that deep beds and much longer residence times could be used with only a small decrease in bio-oil yield [23]. This result is in fact consistent with the work of Liden [24] and others on the rate constant for secondary decomposition of bio-oil. Thermolysis in a deep fluid bed at atmospheric pressure in the temperature range 360-490°C and with gas residence times in the range 2-5 s reportedly gave only slightly lower liquid

TABLE 1  
WFPP data for pyrolysis of maple wood (note that the bio-oil yield is the sum of the organic liquids + water)

Run NO	8	9	4	2
Bed temp., °C	518	532	530	530
Feed rate, kg/hr	2.827	2.191	2.788	1.733
Yields, % m.f.				
Org. liquids	68.24	66.89	58.39	61.83
H <sub>2</sub> O (by G.C.)	10.6	9.7	8.6	9.8
Char	13.25	9.37	17.85	14.73
Gas	9.98	10.02	7.27	7.96
H <sub>2</sub>	0.043	0.043	0.011	–
CO	5.05	5.78	2.48	3.96
CO <sub>2</sub>	4.48	3.68	4.53	3.98
CH <sub>4</sub>	0.24	0.61	0.14	–
C <sub>2</sub> H <sub>4</sub>	0.15	0.20	0.06	–
C <sub>2</sub> H <sub>6</sub> , C <sub>3</sub> 's	0.022	0.037	0.046	–

Note. Pilot Plant Results. Maple – 7% Moisture, – 595 µm, 0.59% Ash, 48.5% C, 6.1% H, 0.50% N(MF). Preliminary Tests.

yields than and similar compositions to those from fast pyrolysis at much higher temperatures (550-600°C) and short residence times (e.g. 0.3-0.8 s).

These results imply that biomass fast pyrolysis can be satisfactorily carried out in the conventional deep fluid bed type of reactor, with the consequent simplicity of scale-up and the advantage of a known and widely used technology.

The RTI process (Fig. 5) [25], implemented in a 10 kg/h pilot plant, employed indirect heating of the fluidized bed (205) using heating tubes (211) immersed in it which also simplifies process operations in so far as the heat supply is independent of the fluidizing gas and biomass feed rates. Furthermore use of longer gas residence times has the advantage that the fluidizing gas to biomass feed ratio can be very low (< 2:1), so that process power requirements are reduced.

High gas flow rates have negative consequences. First, there is a relatively high parasitic power requirement for gas flow and second, there will be increased costs associated with larger condensation/coalescence equipment for the liquid product, assuming their operational efficiency depends on vapour residence times.

### 2.3.3 Dynamotive Process

The RTI process was scaled up several times by *Dynamotive Energy Systems*, through a 100 t/d demonstration

plant (West Lorne) and ultimately to an industrial 200-250 t/d plant (Guelph) (Fig. 6). While these plants met technical performance specifications and demonstrated continuous operation over sustained periods of time (days), the lack of a current market in North America for rough bio-oils utilisation led to their temporary closure.

#### *West Lorne Plant*

West Lorne Development started as a partnership with *Ontario Power Generation (OPG)*, *Magellan Aerospace* (gas turbine manufacturer), *Erie Flooring*, *Wood Products* and *Dynamotive* with support from the Canadian Government under its Sustainable Development Technology Canada (SDTC) program. The idea was to prove concept and replicate across Canada with OPG as a partner. Both technical/developmental as well as logistic/contractual/economic issues were encountered.

The demonstration plant design was a 7× scale-up of a previous 10 to 15 t/d pilot plant. It encountered some technical issues resulting from scale-up of the biomass feeding system, an important technical issue, which led to its replacement by a pneumatic feeding system. There were also some issues around reactor heating; fire tubes versus internal coil heating with a single burner. Eventually the latter proved to be more advantageous.

Another logistic/technical issue that arose related to the biomass feed which contained extremely fine

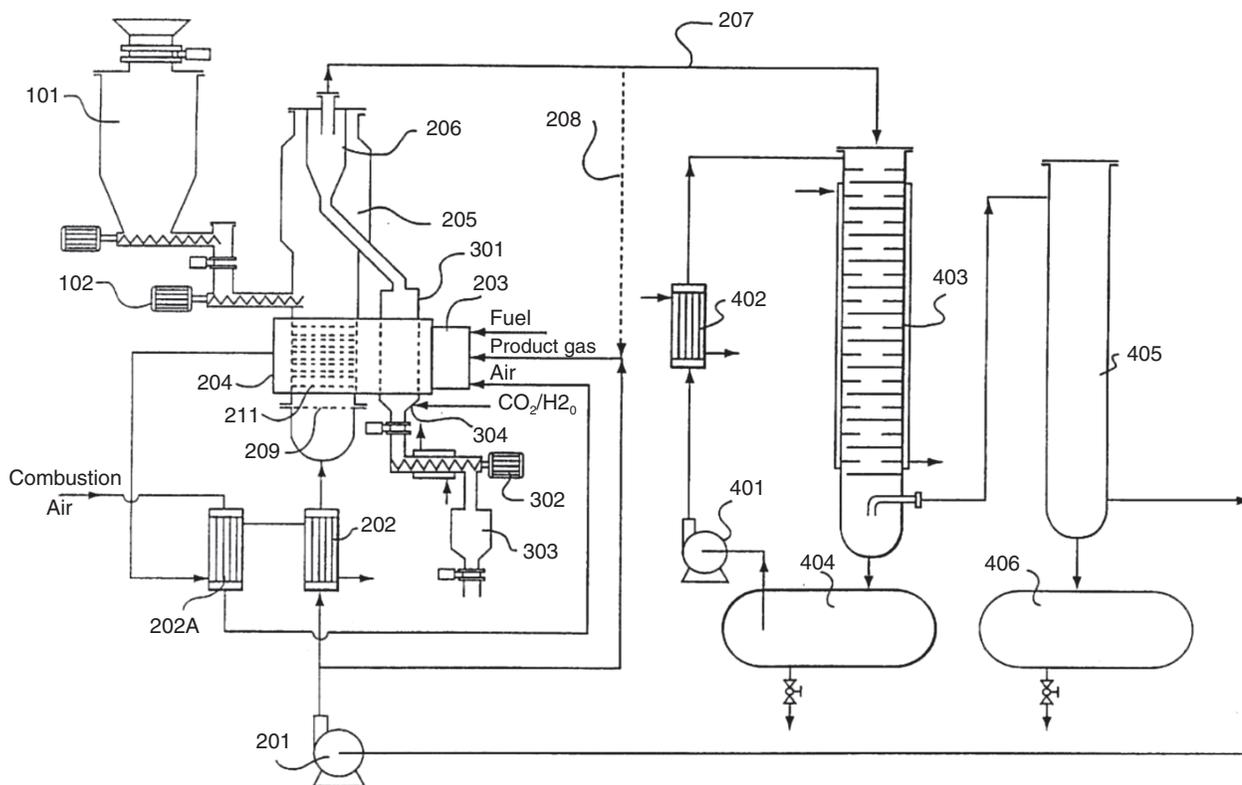


Figure 5  
RTI Process.

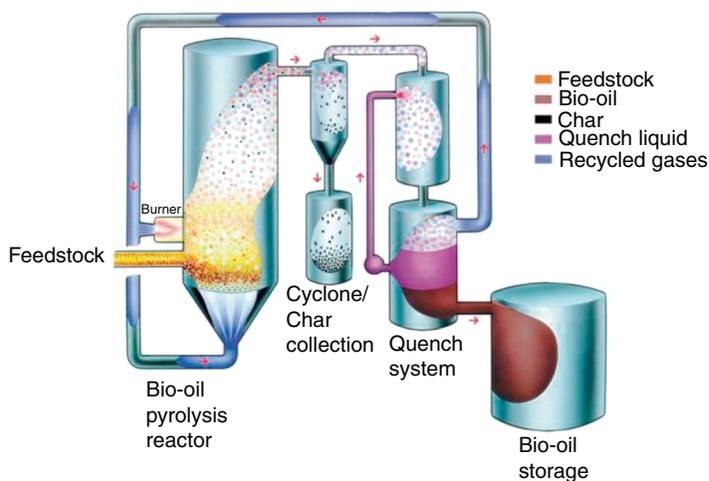


Figure 6  
Dynamotive 200-250 t/d Plant, Guelph, Ontario.

material coming from the sanding operations at *Erie Flooring*. This resulted in micro-char particles that were not captured by the cyclones so that the bio-oil

contained 2-3% of char, some ten times more that obtained from 0.5-3 mm feed particles. This in turn affected the operation of the Orenda gas turbine.

On the economic side, the Ontario Government decided early in the life of the project to de-regulate the Green Energy market and open it to competition, so that OPG was dictated to divest from all its green energy projects as it was a Crown Corporation, leading to withdrawal of OPG, and subsequently *Magellan Aerospace* and *Erie Flooring* from the Consortium.

It was decided nevertheless to upgrade the plant on the basis that it could break based on contracts for specialty products (\$ 800 + per ton) and sales of electricity. However, break-even required a guaranteed minimum biomass supply of 40 t/d/50 t/d. Thus upgrades were completed in 2008, but at that time demand fell drastically with the economic downturn and *Erie Flooring* reduced from 3 to 1 shift so biomass supply could not be guaranteed.

#### *Guelph Plant*

This plant was a fully commercial modular design that was commissioned successfully in 2008. Feed supply was reclaimed biomass from demolition construction wood (MSW) recycling operations. Bio-oil clients were

two large cement companies in the Ontario (which were under environmental orders to use cleaner fuels) as well as other industry in Quebec. However by 2008, the cement plants started to slow down and, in one case, to cease operations.

Furthermore, plans for US market supply and entry were based on tax credits of \$ 1 per gallon that were available to cellulosic fuels (industrial and mobile). On a 200 t/d unit, the tax credit would have amounted to \$10 000 000 per annum to the user of the fuel. However the program was halted for industrial fuels due to abuse by pulp and paper companies resulting from poor drafting of the initial regulations.

Going forward, this illustrates the sorts of challenges to be faced in bio-oil commercialization.

#### 2.3.4 Ensyn Process

Ensyn has developed a variant fluidized bed process based on a circulating fluid bed (*Fig. 7*). It has also been scaled up to several hundred t/d. Pulverized biomass is pyrolyzed by mixing with circulating fluidized sand that has been pre-heated by combustion of the char product of pyrolysis.

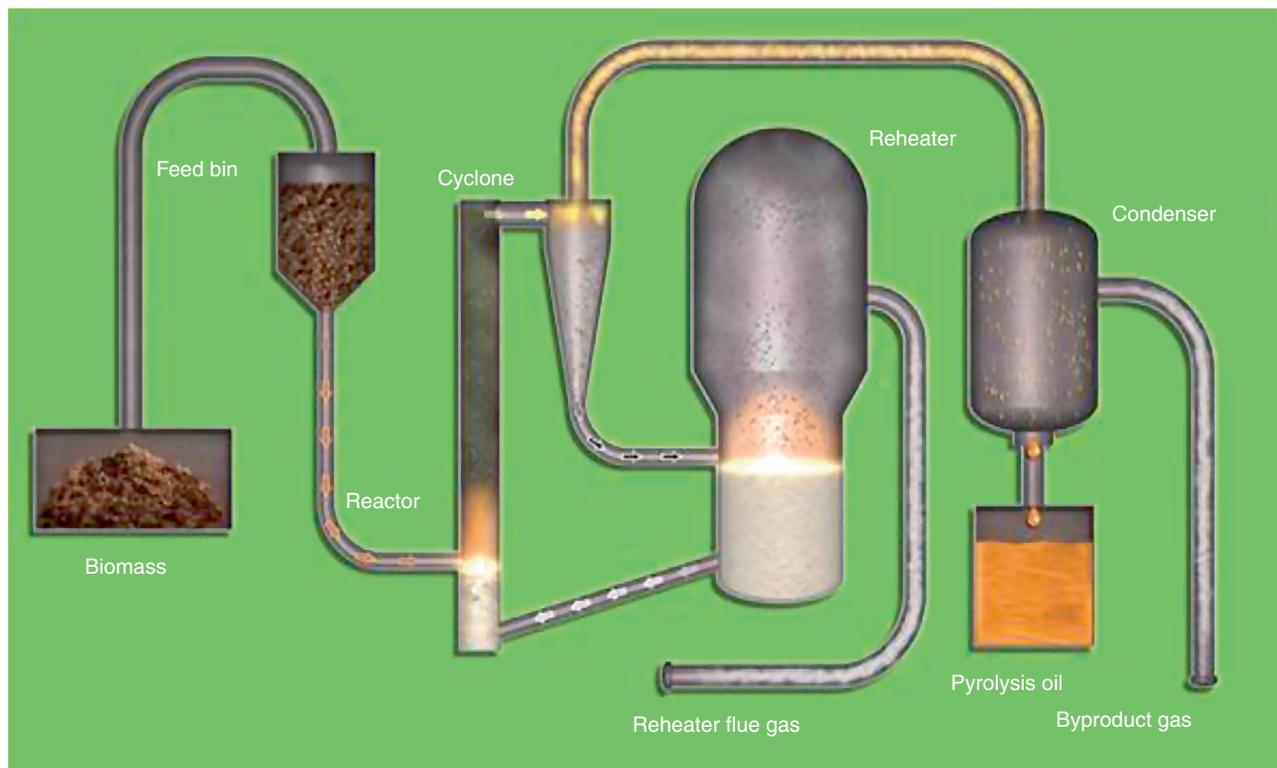


Figure 7  
Ensyn Process [26].

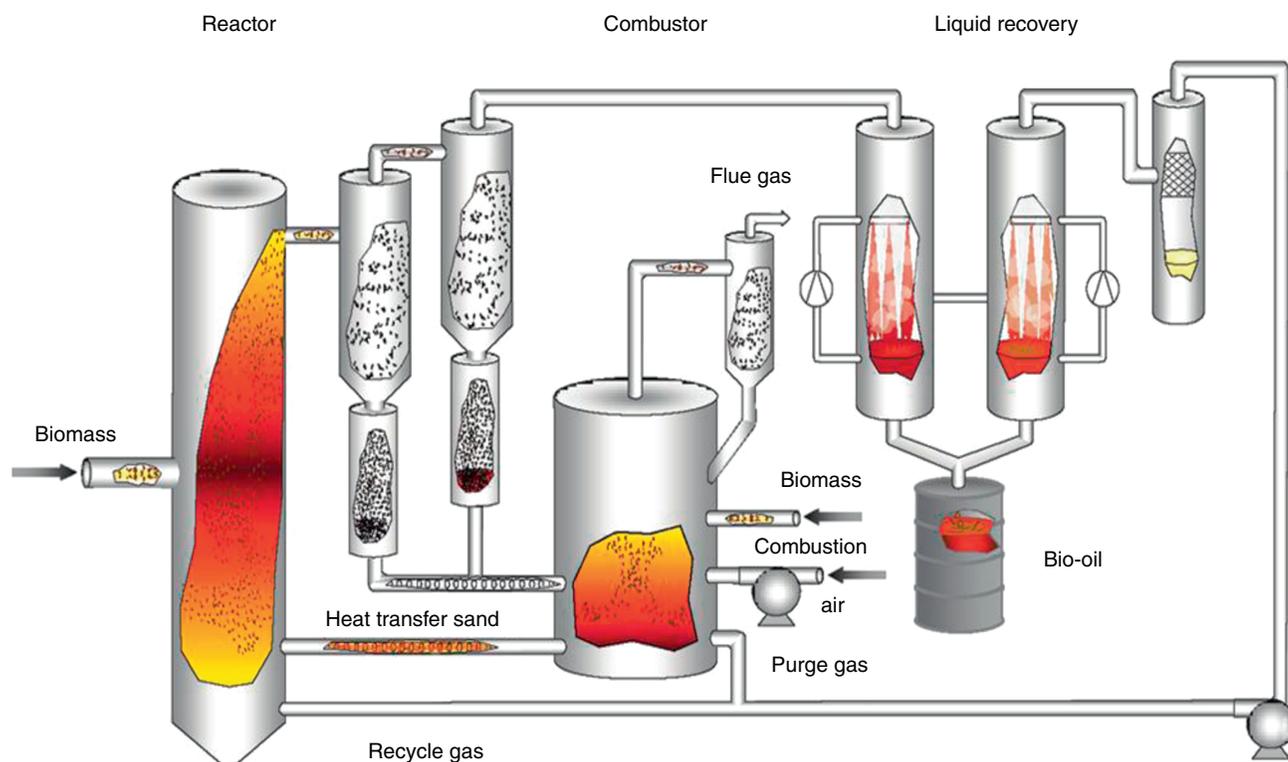


Figure 8  
VTT fluidized bed process [28].

All these processes give comparable product yields, but may differ in complexity, capital and operating costs.

Unsurprisingly, many of the chemicals in bio-oil also occur in wood smoke. In particular, glycolaldehyde, which was identified by Hodge [27] as the principal agent of food browning by wood smoke, through its efficacy in the Maillard reaction, is far more abundant in fast-pyrolysis bio-oils than in wood smoke.

*Ensyn*, working with the *Red Arrow company*, has been able to make a commercial business out of biomass pyrolysis by producing bio-oil for “liquid smoke” applications. Although valuable, clearly this is a rather limited market that cannot support an extensive fast pyrolysis industry.

*Ensyn* commercialized their RTP™ pyrolysis process in the 1980’s and yet designed 7 units in North America, with a size close to 100 t/d. Very recently (World Biofuels Markets, March 2013), *Ensyn* announced 7 new projects under development in Europe, North and South America and Asia, with a bigger size: 150 to 400 t/d.

### 2.3.5 VTT Process

A 20 kg/h circulating bed system has been under development for a number of years at VTT (*Technical Research Centre of Finland*) in Finland. It is illustrated in Figure 8 [28].

Recently (March 2012) *Metso* and *Fortum* power and heat have signed a contract regarding a delivery of a bio-oil production plant to the *Fortum* power plant in Joensuu, Finland. The bio-oil produced in the plant can be used instead of heavy fuel oil, or used as raw material in the chemical industry or for biofuel production in the future. The nominal output of the plant should be 30 MW oil production with a planned production of 50 000 tpy. It results from a collaboration between *Metso* with VTT, *Fortum* and *UPM* since 2007 with a development work based on the research and patents of VTT. The new bio-oil production plant is scheduled for start-up in the autumn of 2013.

Generally bio-oil yields by fast pyrolysis of biomass are highly variable. For instance they depend on the

feedstock and may range from  $\sim 75\%$  for some very clean hardwood feeds through to less than 50% for some straws. Furthermore variability also results from the choice of operating conditions, especially maximum temperature and heating rate as well as gas and solid residence times.

## 2.4 Non-Fluidized Bed Fast Pyrolysis

While fluidized bed processes utilize well established technologies and have been scaled up to several hundred tons per day, several more novel approaches that aim to overcome some of their disadvantages have been introduced in recent years. In particular mention should be made of so-called ablative pyrolysis and the related auger pyrolysis.

### 2.4.1 Ablative Pyrolysis

We have seen that in order to effect rapid heating, large temperature gradients and/or small particle sizes must be employed. However excessive temperature gradients will increase gas production at the expense of organic liquids. An alternative approach is to heat the biomass by contacting it with a hot surface and reducing the thermal resistance by applying a force on the biomass particle perpendicular to the hot surface. The surface layers of the particle are thus subject to very rapid heating and so liquefy quickly. At the same time, forced relative motion of the pyrolyzing particle in a direction parallel to the heating surface will strip off the liquid layer onto the heating surface where its pyrolysis is completed.

This type of process is known as ablative pyrolysis. It takes advantage of the poor thermal conductivity of biomass by confining the liquefaction and volatilization to the exposed biomass surface. There have been several reactor types proposed or demonstrated that exploit this approach, each differing in the method used to apply the perpendicular force.

Probably the first significant technology exploiting the ablative pyrolysis concept was the Entrained FlowVortex Reactor developed at the *National Renewable Energy Laboratory (NREL, formerly SERI)* in Colorado, USA during the 1980's [29]. Here the biomass is pneumatically inject into a tubular reactor along which it spirals and is pressed against the hot wall by the centrifugal forces.

Ideally, fresh un-pyrolyzed biomass surface is continually exposed under these conditions and, indeed, it was originally hoped that this should result in suppressed char yields with correspondingly enhanced liquid yields, but these hopes have not been realised. Yields of liquids, char and gas are comparable to those from fluidized beds. No doubt this is because of two factors: the great speed of low temperature char forming decomposition

reactions and the likelihood that volatilization of the intermediate liquid on the hot surface proceeds in more or less the same way as it does from particle in a fluidized bed; that is to say the liquefied biomass on the hot surface decomposes by the same char forming pathways as in direct pyrolysis of biomass.

Indeed it has been demonstrated recently that that bio-oil cannot be reversibly "evaporated" and this evaporation is always coupled with the formation of char *via* polymerization reactions [30]. When bio-oil was "evaporated" a portion of it was always converted to residual char in an amount dependent on the heating rate, ranging from  $\sim 30\%$  at the lowest rates to  $\sim 8\%$  on a carbon basis, even at highest heating rates in excess of  $10^5\text{C}/\text{min}$ . This is consistent with the observed product yields of ablative pyrolysis methods which do not show a significant decrease in the char product.

It therefore seems that the principal virtue of ablative pyrolysis is that it can, in principle, bypass the need for fine grinding of the feedstock thus reducing the cost of the feed preparation. On the other hand, this must be balanced with the usually higher mechanical complexity and perhaps serious issues of wear of these designs. Scale-up to high throughput industrial units (*i.e.* a few hundred tons/day) is not demonstrated and, may-be, not achievable.

In most designs a large fluidizing gas flow is not required so there is also a potential saving in gas compression costs.

An illustrative recent design is that by *Pytec Thermochemische Anlagen GmbH* [31], in which the perpendicular force is applied by a hydraulic mechanical method (*Fig. 9*). Biomass (optionally large pieces) is fed from a hopper (14) on to a hydraulic element (10) that presses the biomass with up to 200 bar pressure against a hot ( $\sim 750\text{C}$ ) rotating plate (22) on which ablative pyrolysis takes place. Provision is made to separate the char into the receptacle (30).

A 6 t/d (dry biomass) ablative *Pytec* pilot plant has been built and was operated over several years near Hamburg, Germany, on woody biomass. The pilot plant was close coupled with a Diesel CHP plant, burning the bio-oil from the pyrolysis unit to produce electricity in a day-time continuous runs basis [32].

### 2.4.2 Rotating Cone Pyrolyzer

We also mention the rotating cone pyrolyzer using a Rotating Cone Reactor (RCR) developed by *Biomass Technology Group (BTG)*, Netherlands, a reactor that combines features of both ablative pyrolysis and fluidized bed pyrolysis. A recent description of this system can be found in a recent review by Venderbosch and Prins [34].

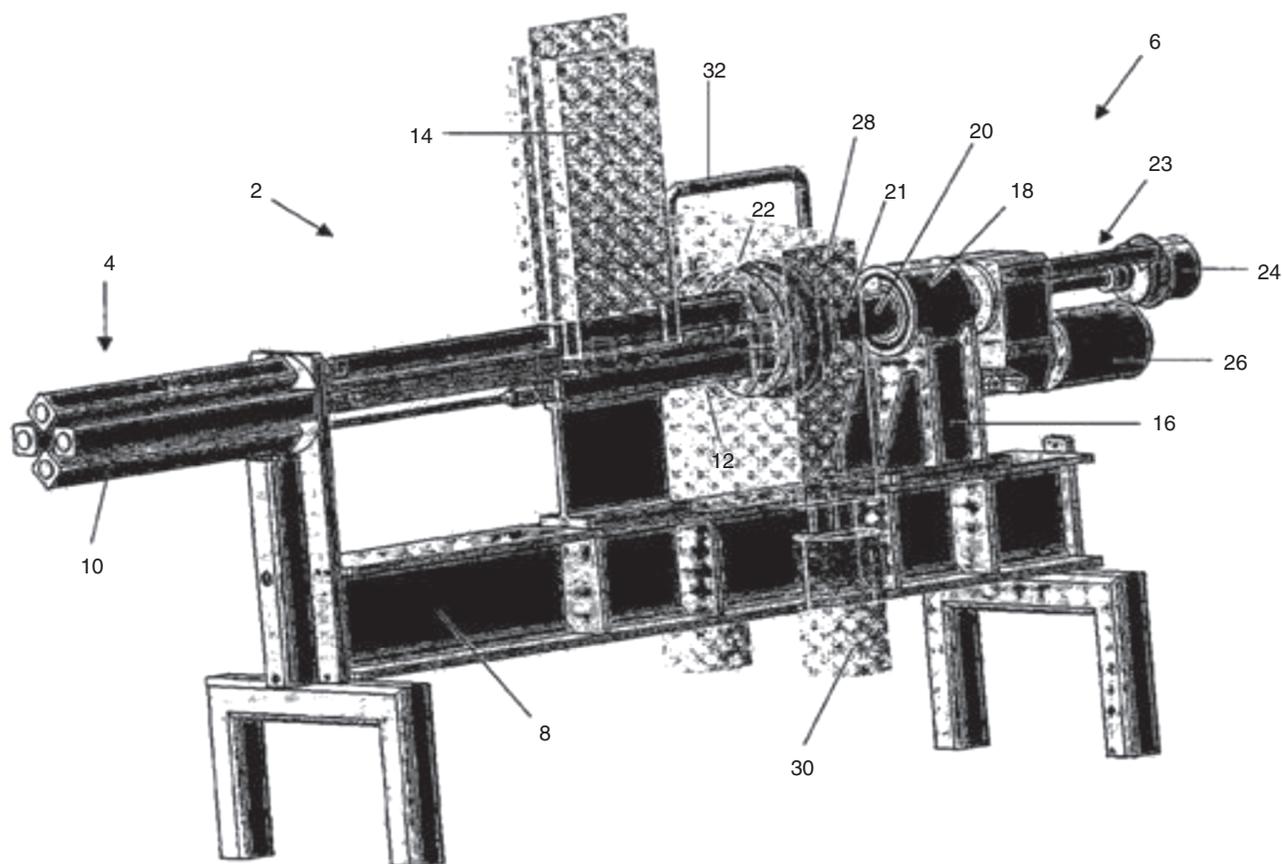


Figure 9  
Pytec ablative reactor [33].

A 2 t/h modular demonstration plant was built in the Netherlands by *BTG* and *Zeton* and was installed in Malaysia in early 2005 and commissioned in fall 2005. It was using empty fruit bunches from a palm-mill from palm oil plantations as a feed and was producing 1.2 t/d bio-oil. As far as we know, this unit was closed. Presently, a 5 t/h plant design is being finalized.

#### 2.4.3 Auger Transported Bed Pyrolysis

A technique related to ablative pyrolysis is “auger pyrolysis” where the biomass is transported along a hot tube by mechanical displacement using twin augers. This is essentially a type of transported bed reactor as the twin-auger is effectively a series of sealed pockets that advance the feed to the discharge port. Heat may be supplied by wall heating of the auger tube barrel or by circulating pre-heated sand that is mixed with the biomass.

Liquid yield are somewhat lower in these approaches but it seems suitable for small-scale pyrolysis

operations. However it should be noted that a recent report [35], suggests that it is possible to obtain comparable bio-oil yields to more conventional fast pyrolysis methods under suitable operating conditions. Furthermore the physicochemical characteristics of the bio-oil have also been found [36], to be similar to those produced by other methods.

Because of its compact nature it is especially favoured for small mobile pyrolyzers, [37] that are moved to the site of the feedstock and where throughput is of the order of a few tons per day. On the other hand, since economies of scale are not available, the economics of small-scale pyrolysis, especially for fuel applications, are not clear.

Another development related to the auger transported bed technology is the twin auger reactor from *Lurgi*, developed and tested in the *bioliq*® process by the *Forschungszentrum Karlsruhe (FZK)*, recently merged with the *Karlsruhe University* into the *Karlsruhe Institute of Technology (KIT)* [38]. More information is available

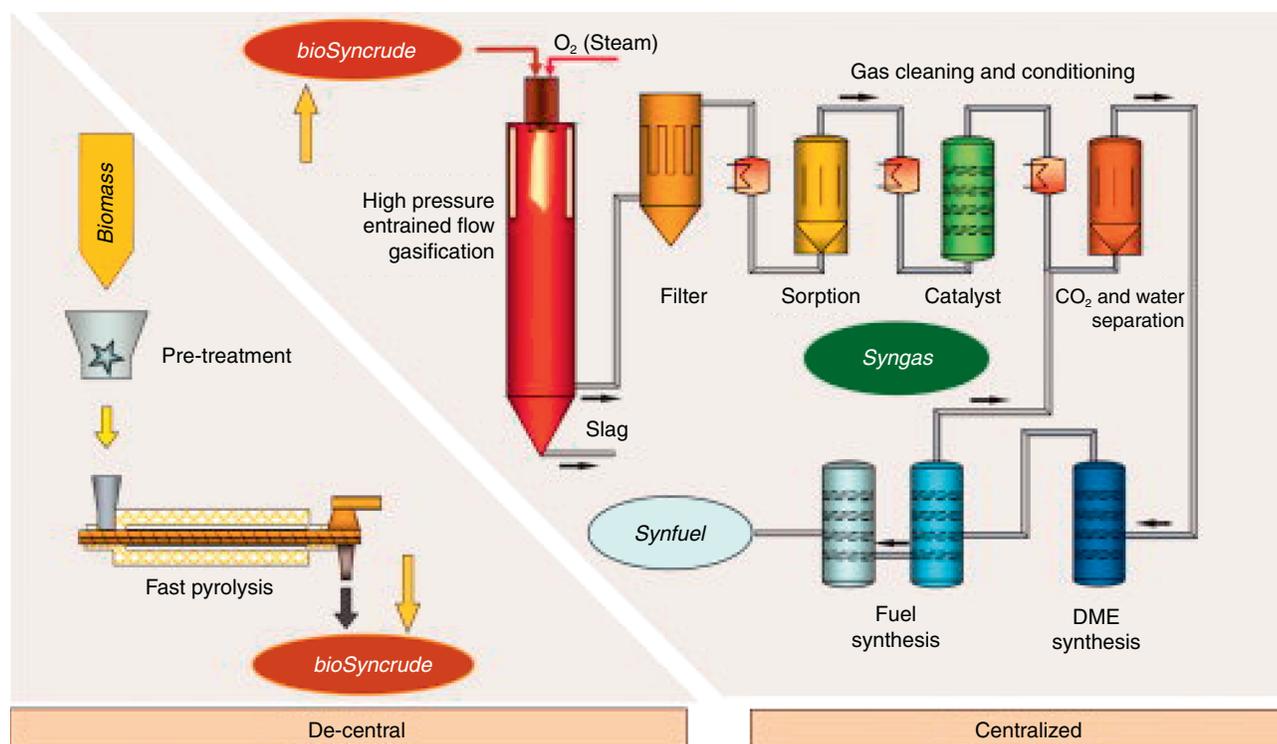


Figure 10

Bioliq® process for synthetic biofuels production [40].

on *KIT* and *bioliq* web sites [39]. This is a peculiar application of pyrolysis for biomass gasification in which the overall goal is specifically to densify the biomass to reduce its transportation costs and simultaneously convert it to a feedstock suitable for high temperature gasification and subsequent Fischer-Tropsch conversion to high quality fuels or for methanol conversion that can be used as a rough feedstock for gasoline synthesis (Fig. 10). Since the gasifier in question accepts both char and bio-oil as inputs, liquid yields are largely immaterial as the gasifier feed is actually a slurry of bio-oil and char so that the bio-oil/char ratio is largely irrelevant.

These types of reactors have been demonstrated scales up to about several tons of tonnes per day (*i.e.* 0.5 t/h or 2 MW(th)) for the flash pyrolysis *bioliq*® pilot plant which also uses twin screw auger pyrolysis. Mechanical complexity, wear and their attendant issues are potential matters of concern.

## 2.5 Bio-oil for Energy Applications

So far a viable economic business using bio-oil as an energy source has not been established in spite of

considerable interest in the technology over the past twenty years. This appears to be primarily due to properties of bio-oil as a fuel rather than its production technology. There are several characteristics that make the routine usage of bio-oil for energy purposes problematic. These include:

- high acid number and consequent high corrosivity;
- risk of deterioration by polymerization and/or phase separation on prolonged storage if exposed to air;
- presence of microscopic char particles;
- incompatibility with petroleum based fuels that restrict flexibility of usage, transportation and handling;
- poor thermal stability above, *i.e.* 150°C.

These issues have been discussed in some detail by Scahill *et al.* [41].

Microscopic char is perhaps the most important limiting factor in the direct combustion of bio-oil in engines where it has to be sprayed through fine nozzles. Shihadeh [42] found that abrasion of nozzles was a major problem and even after passing bio-oil through a 10  $\mu\text{m}$  filter, it generated deposits on piston head and cylinder surfaces and in situ growth of solids in the nozzle of a Diesel engine. This microscopic char seems distinct from the

macroscopic char that is a primary pyrolysis residue of the biomass fed and, unlike which, cannot be removed by cyclones economically. Indeed, as discussed above, it appears likely to be an intrinsic product of pyrolytic volatilization of bio-oil.

Consequently direct use of bio-oil as a liquid fuel has been practically restricted to combustion in boilers and kilns. A recent discussion of such an application has been reported by Solantausta *et al.* [43].

Several more comprehensive recent reviews of these technologies and others not mentioned here that have been studied at various scales are available, for instance those of Butler *et al.* [44], Venderbosch and Prins [34], and Mohan *et al.* [45].

The apparently limited economic opportunities for direct use of bio-oil as a liquid fuel have motivated a search for methods of valorizing it.

It is important for the economics of fast pyrolysis that a suitable use be found for the char product. Proposals have been made to use for use as biochar but it is not clear whether there is or will be a viable market for it, [46]. It could also be used as a solid bio-fuel to replace coal or petroleum coke or gasified, possibly to produce bio-hydrogen.

### 3 CATALYTIC PYROLYSIS

The success of the *Mobil* MTG process, [47], for converting methanol to hydrocarbons over medium pore zeolites like ZSM-5 led to suggestions for similarly converting bio-oil vapours to hydrocarbons. An early example is the *Occidental Research Corporation* process patented by Frankiewicz in 1981, [48] in which it was suggested to pass the vapours from a pyrolyzer over a bed of zeolite ZSM-5.

Although the C:O ratios in both methanol and biomass/bio-oil are approximately 1:1, the relative hydrogen content in bio-oil is considerably lower (bio-oil is typically approximately  $\text{CH}_{1.87}\text{O}_{0.75}$ ). Diebold and Scahill [49], reported in 1988 that ZSM-5 converted bio-oil vapours largely to alkylated benzenes. However this is accompanied by considerable coke formation, implying inefficient use of renewable carbon, with rapid catalyst deactivation on account of the low H/C ratio of bio-oil.

This suggests that such processes might be most efficiently carried out using some kind of circulating fluid bed technology where the fluidized bed is constituted of the catalyst rather than inert sand. More recently *KiOR Inc.* in Texas, USA, [50], has announced progress in the scaling up of this kind of technology, see Figure 11. It is envisaged that the crude hydrocarbon product is subsequently hydrotreated in a conventional oil refinery.

Very recently (fall 2012), *KiOR Inc.* announced the start-up and the beginning of the production of their *Colombus Industrial Demo* unit in Mississippi using their BFCC process with a capacity of 500 t/d bone dry biomass with a yield of 67 gal (or  $0.2536 \text{ m}^3$ ) /t bone dry biomass, roughly corresponding to a production of  $42\,000 \text{ m}^3/\text{y}$  on a 330 d/y basis.

A second industrial type plant is scheduled in Natchez, Miss 1500 t/d bone dry biomass.

Since a few years *RTI International (Research Triangle Institute)*, nothing to do with the RTI process previously discussed), has also developed such a catalytic process, currently at small scale pilot plant level (0.1 to 0.35 kg/h) [51].

Recently (October 15, 2012), *RTI International* announced that it launched construction of a new biomass pyrolysis research facility that “will house a biomass pyrolysis reactor to further extend *RTI*’s biofuels research efforts”... “to produce a suitable pyrolysis oil from locally-available biomass resources, such as pine trees, that can be substituted for petroleum in existing oil refineries”. In this new centre, *RTI* will focus “on developing a process for the catalytic pyrolysis of biomass, supported by lab scale testing of catalysts and the design, construction and operation of a demonstration unit” (1 ton a day of biomass to produce up to 60 gallons of pyrolysis oil per day) “that produces pyrolysis oil from biomass materials such as woods chips”.

Annelotech is also developing a catalytic pyrolysis process from the *University of Massachusetts*, with the aim of producing chemicals from biomass, especially aromatics (benzene, toluene and xylenes) [52].

### 4 CATALYTIC HYDROLYSIS

Catalytic hydrolysis represents an alternative approach to catalytic pyrolysis. It is also most suited to fluidized bed pyrolysis. Pyrolysis is carried out in an atmosphere of hydrogen rather than an inert gas and the bed is replaced by a transition metal catalyst.

Radlein *et al.* [54], showed that by replacement of inert sand in an atmospheric pressure bubbling fluidized bed by various Ni based catalysts, it was possible to convert most of the bio-oil in situ, into low-molecular weight, mostly gaseous hydrocarbons, even at very short gas residence times.

Recently a new process,  $\text{IH}^2$ , designed at *GTI (Gas Technology Institute)*, Illinois, USA, reported a modification of this process in which the hydrolysis was carried out under pressures in the range 7-34 bar [55]. Under the elevated pressure the average molecular weight of the hydrocarbon product increased such that

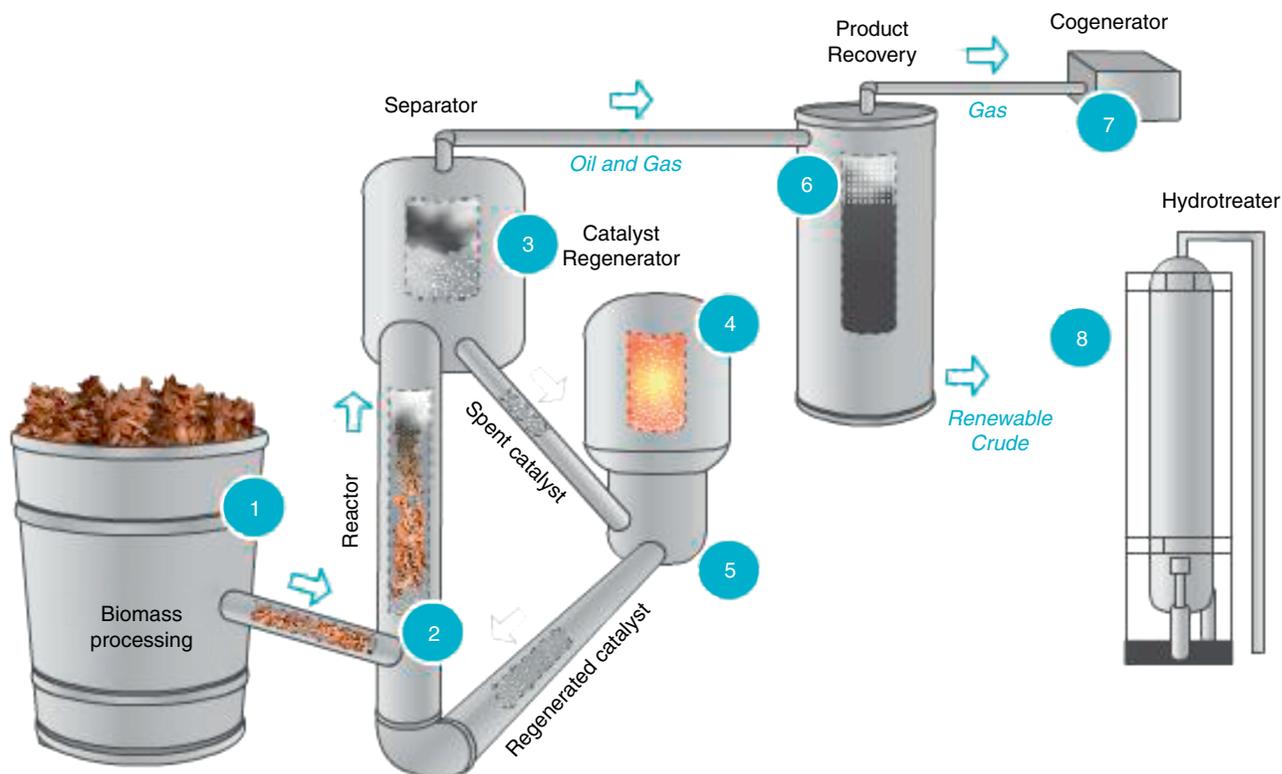


Figure 11  
KiOR process [53].

a substantial portion of it was comprised of light hydrocarbon liquids. The lighter  $C_1$ - $C_3$  gases can be subsequently reformed to generate the relatively large amounts of hydrogen required. The process is under a development phase with a 0.5 kg/h bench unit installed in 2009 and a new 50 kg/d pilot plant installed in early 2012 and currently operated to develop the process. The target is full scale commercial deployment for early 2014. This development industrial looks very fast regarding the complexity of such integrated processes.

The system is also very complex as it is fully integrated (hydrolysis and reforming) and no doubt technical challenges like feeding biomass solids into the pressurized pyrolyzer under hydrogen must be overcome. All this suggests that the capital costs will be high, so the question arises of the scale at which it would become economical, a question that arises specifically because of the intrinsic diffuse nature of biomass resources.

## 5 HYDROTREATING

As we have seen, many distinct technologies have been developed for production bio-oil by fast pyrolysis. Unfortunately they have led to very few commercial

successes, principally because no significant market has been found for bio-oil so far. Transformation into drop-in transportation bio-fuels appears to be an attractive route to provide such an outlet and to increase the valorization of the bio-oil. Some recent development in this direction are outlined below.

The main challenges in upgrading bio-oils are:

- to enhance the very poor thermal stability of bio-oil (generally not stable above 150°C);
- to remove its acidity and metal content;
- to get a good separation of aqueous phase and organics without re-polymerization;
- to make upgraded products miscible with hydrocarbons.

Most of these challenges can be overcome by reducing the oxygen content to a low or very low level. Thus, an alternative approach that decouples pyrolysis from upgrading is the direct catalytic hydrotreatment or hydrocracking of bio-oil. This has been a subject of study for a long time. Many recent and more comprehensive reviews of the progress made in this aspect are available [56, 57].

Most of the works deal with a two steps high pressure HDO (up to 20 MPa) of the whole bio-oil to

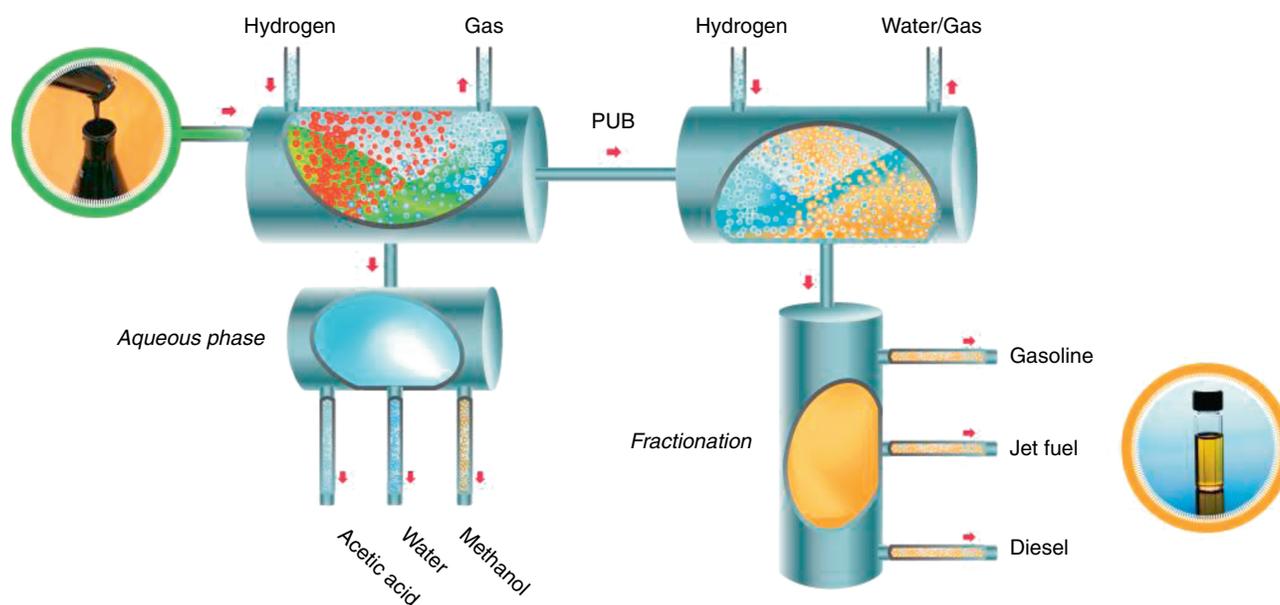


Figure 12  
Schematic of BINGO process.

transportation fuels: the 1<sup>st</sup> step is usually operated at a low temperature (*i.e.* about 250°C) and high hydrogen pressure in order to stabilize the most reactive oxygenate compounds of the bio-oil and to avoid polymerization. This is usually performed on a noble metal (*i.e.* Pt, Pd, Ru, etc.) on carbon support which presents a good chemical stability. Noble metals on ZrO<sub>2</sub>, as well as NiMo or CoMo on alumina or alumina/silica catalysts are also used.

The second step may use the same catalysts but at much higher temperature (*i.e.* 350 to 400°C) and high hydrogen pressure in order to hydrotreat almost all the remaining oxygenate compounds to hydrocarbons.

All these hydrotreating approaches are generally using a very low space velocity, resulting in large size hydrotreating reactors at industrial scale, with a high hydrogen consumption (*i.e.* 4-7 wt% on bio-oil), removing most of oxygenate compounds to H<sub>2</sub>O. They usually mainly produce gasoline and jet-fuel. They also result in a moderate liquid hydrocarbon yield, close to 20 wt%. It makes this “conventional” hydrotreating approach quite expensive for investments as well as for operating costs. The catalyst life is generally quite low.

Nevertheless hydrotreating is considered as a promising route to upgrade bio-oils, in so far as it is possible to minimize oxygen content when minimizing hydrogen

consumption, investment and operating costs, using as mild operating conditions as possible and optimizing the final liquid hydrocarbon yield.

Recent developments include two stage upgrading processes and are developed to reach these technical challenges, as schematically illustrated in Figure 12 [58]. This is the example of a two stage hydroprocessing process, currently called BINGO process, presently being developed by *Dynamotive* (DYMF) and *IFP Energies nouvelles*, that features a relatively low hydrogen consumption, which is an important requirement given the current rather high cost of hydrogen, with a high hydrocarbon liquid yield close to 300 L/t dry biomass. The process is more oriented towards middle distillates (*i.e.*, jet fuel and Diesel) than toward naphtha/gasoline.

Comparable technologies include the process of *Envergent Technologies* [59] which is a joint venture of *Ensyn Corp* and *Honeywell's UOP*.

A very important work was also performed in the field of flash pyrolysis bio-oil hydrotreating and conversion of the upgraded bio-oil, successfully co-processed with a petroleum feedstock in small a Fluid Catalytic (FCC) pilot plant to produce gasoline. This study was performed within the European joint project BIOCUP [60]. A lot of information related to the BIOCUP project, including many presentations and papers, can be found on the BIOCUP web site [61].

## CONCLUSIONS

The kinetics of pyrolysis of biomass suggested that its thermal decomposition proceeds by various parallel pathways the most important of which being a low temperature, low activation energy pathway producing mainly char and gas, a high temperature, high activation energy pathway producing mainly condensable vapours and liquid aerosols. In order to maximize liquid yields, it was therefore important to heat the biomass rapidly to a suitably high temperature. However this is problematic since wood presents a poor thermal conductivity. Thus rapid heating of biomass requires small feed particle sizes for uniform particle heating and for which fluidized beds offer an efficient reactor type. While fluidized bed processes utilize well established technologies and have been scaled up to several hundred tons per day, several more novel approaches that aim to overcome some of their disadvantages have been introduced in recent years. They include so-called ablative pyrolysis and the related auger pyrolysis methods and can tolerate a wider range of particle sizes through the use of predominantly particle surface heating.

Nevertheless these novel approaches are not fully demonstrated at industrial level and the well established non circulating and circulating bed fluidised bed processes, yet remain the only industrially demonstrated processes.

The use of bio-oil as a renewable liquid fuel is hampered by its poor physicochemical properties and the market is not yet really available for direct energy applications. Currently, economic prospects for liquid fuel applications are thought to depend on its conversion to high grade hydrocarbon fuels like gasoline, Diesel or kerosene, or chemicals such as olefins or aromatics, which are currently in a developmental stage. Clearly, a desirable feature of any upgrading technology is that it should be able to accommodate a broad distribution of biomass residue types, and hence of bio-oil properties, in order to be economically feasible and technically operable. One interesting feature is the ability to co-process at least partially upgraded bio-oils with petroleum feedstocks with a dual main advantage: reducing the overall investment as well as the operating cost and using existent refining processes in existing petroleum refineries.

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