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MODERN METHODS OF THERMOCHEMICAL BIOMASS CONVERSION INTO GAS, LIQUID AND SOLID FUELS

NOWOCZESNE METODY TERMOCHEMICZNEJ KONWERSJI BIOMASY W PALIWA GAZOWE, CIEKŁE I STAŁE

Abstract: Biomass utilization through direct- or co-combustion with coal, based on coal, hydrogen and oxygen compounds' chemical energy conversion into heat in boilers, is simultaneously the cheapest and - according to experts - economically least effective solution. In case of heat and electricity production in cogeneration process in biomass fueled heat and power stations (wood, straw, energetic plants, RDF etc), investment costs are little higher, but considering fluidized combustion, combined heat and power (CHP) cogeneration systems, combined heating cooling and power generation (CHCP) trigeneration systems, ORC systems etc. the efficiency increases as well as the economical and ecological effects improve. Therefore, the most effective economical, and technical alike, methods of biomass conversion are: partial oxidation, gasification, thermal decomposition (pyrolysis) and biocarbonization processes. This paper includes review of present modern technologies taking advantage of these processes in gas, liquid and solid fuels production.

Keywords: biomass conversion, pyrolysis, fuels

The utilization of biomass for heat production in direct or co-firing processes is economically the least profitable manner of converting chemical energy into useful energy. A more effective way is conversion conducted in cogeneration and trigeneration systems, because of their superior proficiency. However, conversion into liquid or gas biofuels is the most profitable method. Figures 1 and 2 presents all biomass conversion methods - into thermal and electrical energy as well as into solid, liquid and gas biofuels [1, 2].

Thermal decomposition of biomass

Thermal decomposition of biomass, which is an anaerobic-atmosphere, endothermic process, leads to arise of three products:

- biocarbonate - charcoal while from decomposition of wood,

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- oil - which is a hydrocarbons mixture,
- gas - also a hydrocarbons mixture, but gaseous, with calorific value ca 12 MJ/kg.

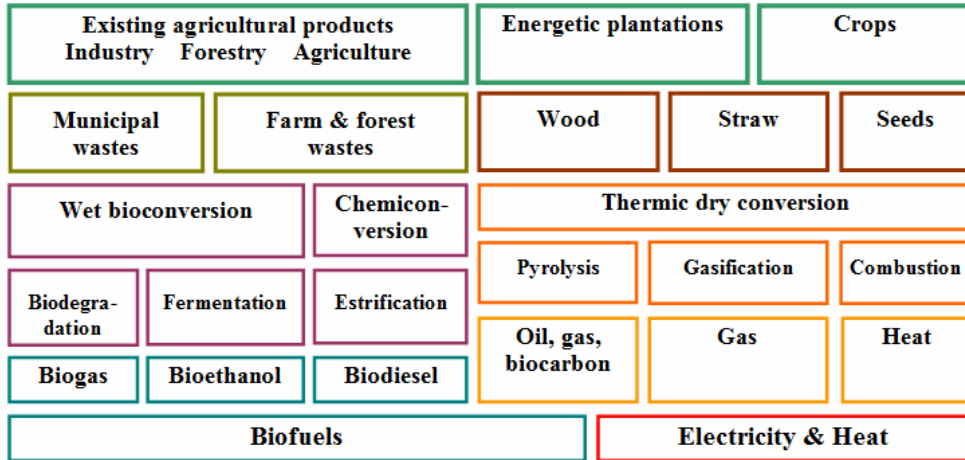


Fig. 1. Sources and types of biomass and methods of their conversion [2]

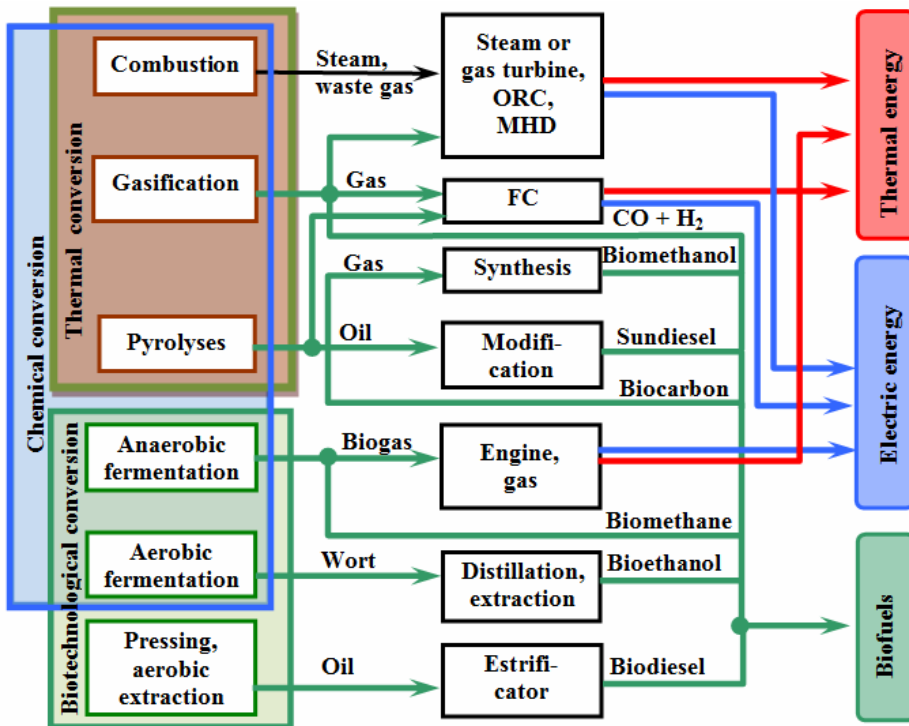


Fig. 2. Review of biomass conversion methods into useful electrical, thermal energy and into solid, gas and liquid biofuels

Its composition depends on temperature of biomass decomposition and so, eg for temperature 482°C/926°C in percentage (by volume) it is following: 5.56/32.48 H₂, 12.34/10.45 CH₄, 33.50/35.25 CO, 3.03/1.07 C₂H₆, 0.71/2.43 C₂H₂. Inflammable gasses are present in this mixture in an amount of 54.97% for temperature 482°C or 81.68% for 926°C [3].

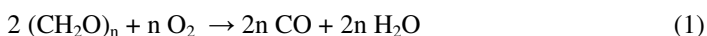
Proportions of gasses, oil and biocarbonate in degradation products depend on accession rate of temperature, decomposition time, temperatures and pressure. At a fast thermal decomposition process rate, over 65% of biomass becomes gas (gasification), at an average rate - over 70% of biomass transforms into oil (pyrolysis) and it is possible to receive over 35% of biocarbonate (biocarbonisation) at slow decomposition rate. As it turns out, one more factor has an influence on thermal decomposition of biomass, namely catalyst.

In a technology used by Alphakat GmbH, a company in Buttenheim near Nürnberg, thanks to Al-Si zeolite addition into biomass (carbon, straw and deposits from sewage-treatment plant of municipal) during thermal decomposition process, it became possible to shift the direction of reaction into receiving more liquid products, at the cost of smaller amounts of gaseous and solid products.

Thermal decomposition of biomass starts at as low as 200°C, while the overhead value of temperature is not limited (it can even be as high as plasma temperature). The final products are charcoal and pyrolytical gasses. In room temperature, ca 30% (by weight) of pyrolytical gasses are condensed in form of a mixture of oil, alcohol, hydrocarbons and other organic compounds.

Gasification

Taking into account the installation reliability, the temperature of gasification and partial pyrolysis should not surpass 950°C. This temperature is adjusted by inserting certain amount of water steam into the gasificator, which endothermically reacts with the residue left after the pyrolysis process - the charcoal:



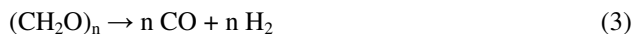
Produced gas includes a mixture of primary pyrolytical and water gas and its caloric value grows ca 50% higher and is now at a level of ca 11 MJ/kg [3]. Gasification process is conducted in closed ordinary reactors or in reactors with a fluidal field. Received gas, mainly hydrogen and carbon oxide, can be burned in the steam boiler, and the produced steam may supply turbines in a thermal power plant. In a different scenario, it is possible to employ gas from biomass directly in the gas turbine and to receive 1450 kW·h of electrical energy from one tone of biomass e.g. wood (calorific value 16.2 MJ/kg). Gas received from biomass gasification can also be converted into electric power directly in fuel cells. Gasificators with solid packing are applied at forces from about ca 1.5 MW at co-current match, and ca 2.5 MW in countercurrent gasification process. Fluidal reactors can process up to ca 15 Gg/h of dry biomass, creating power from 25 MW up to ca 100 MW.

Thermal biodegradation jointed with hydrogenation

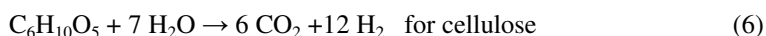
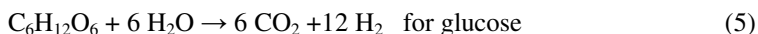
It is also a pressurized oxygen-free biomass gasification process, but lead in such a manner that the final product contains as large amount of liquid hydrocarbons as possible.



The reaction is carried out in two stages. During the first period, synthesis gas emerges, which then reduces biomass into liquid hydrocarbons:



It is also possible to obtain the hydrogen for hydrogenation through hydrothermal gasification of wet biomass in approximately-critical water conditions ($T_c = 374.15^\circ\text{C}$, $p_c = 22.14 \text{ MPa}$). The reaction is following:



During hydrothermal gasification process, hydrogen, carbon oxide and considerable amounts of methane and superior hydrocarbons are produced. There are two methods to carry out this transformation:

- low-temperature $T = 350\div 600^\circ\text{C}$ with ZrO_2 catalyst,
- medium-temperature $T = 500\div 800^\circ\text{C}$ with KOH , KHCO_3 , K_2CO_3 catalysts.

Conversion of biomass into liquid biofuels is, according to specialists [4], most economically reasonable. In their statement, profits obtained from biomass conversion into heat, electricity or liquid fuels are equal to:

$$\text{heat} : \text{electrical energy} : \text{liquid fuel} = 1 : 3 : 9 \quad (7)$$

Thus far, the price of fuels was not the motor driving the search for new technologies. Presently, when situation has changed and the meaning of biofuels has increased, it is possible to forecast a raise of interest in biofuel production through biomass thermal biodegradation.

Biomass pyrolysis

Pyrolytic thermal biomass decomposition is a complex process in which primary simultaneous reactions occur: dehydration, isomerization, aromatization, carbonization, oxidation and other. Secondary reactions also occur eg thermal water decomposition into synthesis gas, cracking, condensation etc. Depending on technological parameters of the process, mainly temperature and its rise rate, the following products emerge: water steam, carbon oxides, aliphatic and aromatic hydrocarbons, tars, polymers, hydrogen and carbon. Table 1 presents the variability of composition and individual components participation in products of pyrolytic wood decomposition in the function of temperature.

Table 1
Composition of gas gather from free distillation of dry biomass (timber) in function of temperature

Process	Temp.	H_2	CO	CO_2	HC
	[$^\circ\text{C}$]				
Dehydration	155÷200	0.0	30.5	68.0	2.0
Carbon oxides (oxidation)	200÷280	0.2	30.5	66.5	3.3
Hydrocarbons emerge (HC)	280÷380	5.5	20.5	35.5	36.6
Production of hydrocarbons	380÷500	7.5	12.3	31.5	48.7
Dissociation	500÷700	48.7	24.5	12.2	20.4
Emerge of hydrogen	700÷900	80.7	9.6	0.4	8.7



Biomass biocarbonization

Energy plantations and other biomass sources must be placed in a radius of 100 km from energy adaptive plant. Because of big cubature and small specific gravity, transport of biomass through far distances is unprofitable. A certain solution of this problem is biomass conversion into biocarbon, which is pure charcoal and in which concentration of energy is considerably greater than in biomass. Indeed, density of such carbon is not equal to hard coal, but coverage of its profitable transport range for thermal power plants is still contained within Polish territory.

Biocarbon, just as charcoal, is received during biomass warming without access of air. It is possible to carry out this process in closed reactors with overcoat heating



First attempts at starting-up a commercial Polish installation of biocarbon production in Wodnyia near Elbląg have ended in a failure [5]. An accomplished installation, manufactured by the same planners in Sedziszow is presented in Figure 3 [6-8]. It remains to be seen whether experience gained in Wodnyia will prove useful.



Fig. 3. Installation of BIOwęgiel® (biocarbon) production in Sedziszow (under construction) [6-8]

Additional advantages of biocarbon as a fuel are as follows: capability of incinerating in a traditional carbon boiler, without necessity of modernization, lack of sulfur in it and a possibility of obtaining a green energy certificate and additional profit from increment emissions trading (according to CO₂ limitation emission programme).

Pyrolytic RDF recycling installation

An example of flash-type pyrolysis is a vacuuous installation for conversion inflammable fractions of waste materials called RDF (Fig. 4) [9, 10]. From 1 kg of waste it is possible to receive ca 0.23 kg of recovered fine-grained carbon at temperature $t = 760^\circ\text{C}$ and gas mixture of hydrocarbons at temperature $t = 510^\circ\text{C}$. Liquid fuel was obtained after fast cooling to ca 80°C , in order not allow a reaction with carbon to occur.

After multistage cleaning-up the gas was transferred for industrial utilization. Part of it was turned back to sustain the pyrolysis process. The final effect of RDF pyrolysis was: ca 10% (by weight) of water, 20% of carbon, 30% of gas and 40% of liquid fuel. Recycling



efficiency of carbon production at calorific value 20.9 MJ/kg and ca 30% contents of ash, equals ca 7.5%, in dry mass calculation. In case of liquid fuel, the equivalent values were following: calorific value - 24.4 MJ/kg, contents of ash from 0.2 to 0.4% and production efficiency - 22.5% by weight.

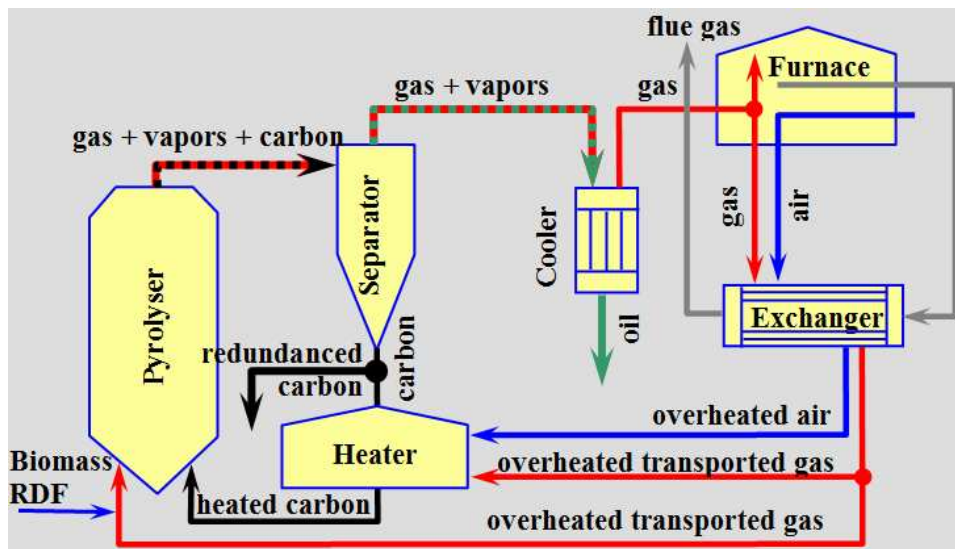


Fig. 4. Scheme of technological line of RDF pyrolytic conversion into liquid fuels

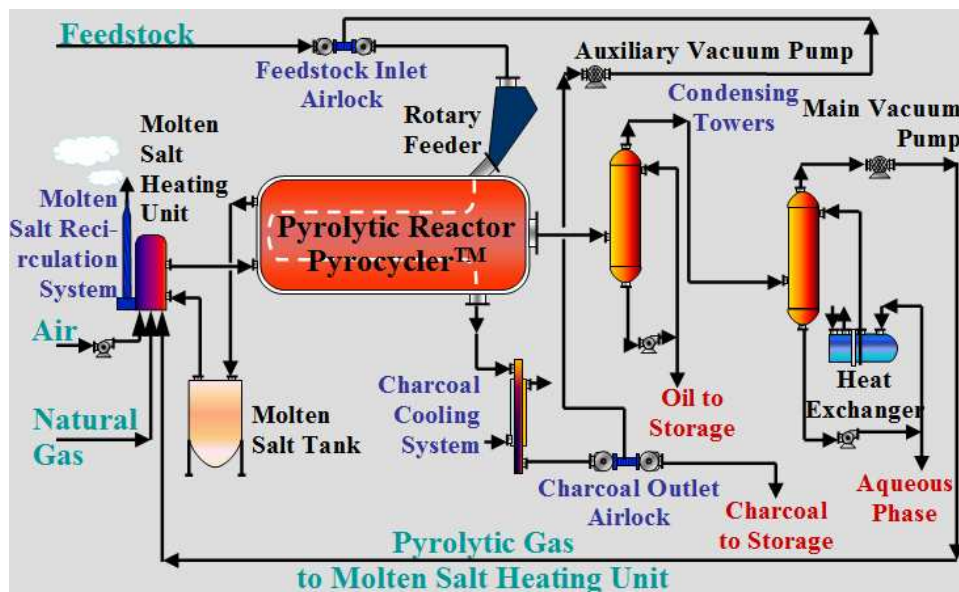


Fig. 5. Technological scheme of Pyrocycling™ Process [11]

Pyrolytic Pyrocycling™ installation

Pyrocycle™ Process was developed by a canadian-dutch firm. The raw material for the processing is bark from soft trees, obtained at a sawmill, dried outside. Composition of raw material is approximately: 31% (by volume) balsam fir (*Abies balsamea*), 55% (by volume) - white spruce (*Picea glauca*) and 14% (by volume) - black spruce (*Picea mariana*). Average humidity of raw material at inflow to the reactor is 10% (by weight). Approximated analysis of the product is: 74.8% volatile parts, 22.3% related carbon and 2.9% ash. Technological scheme of Pyrocycling™ Process is present in Figure 5.

Other examples of pyrolytical technologies

Table 2 contains majority of most popular applicable pyrolytical technologies assembling biomass into useful energy.

Table 2

Juxtaposition of most popular and newest pyrolytical technologies [12]

Technology	Producer	Material	Efficiency	Temp.
			[kg/h]	[°C]
BTG Flash Pyrolyse	BTG Biomass Technology Group [13]	Biomass	250, 5000 (Starting-up Installation)	500
Pyrocycling Process [15, 16]	Pyrovac Group Inc., Ecosun b.v. [14]	Biomass	3500	475
ENTECH Pyrolytic Gasification System	ENTECH Renewable Energy Technologies PTY Ltd. [17]	Biomass & Organic Wastes	Series of Types 200 - 36000	500
Waste Gas Technology	Waste Gas Technology Ltd. [18]	Dried Sludges	500	750÷850
Ragailler Dry Distillation	RATech [19]	Municipal Wastes & Biomass	n.a.	450÷560
HD-PAWA-THERM	UC Prozesstechnik GmbH [20]	Sludges	n.a.	600÷700

Conclusions

Biocarbon, liquid biofuels and gas (water or generator gas) are the products of thermal decomposition of biomass. Transport, storage and farthest processing are economically and ecologically more profitable, due to boosted density of energy in these processed biofuels, than rigorous biomass, which is light and has small calorific value.

Methods of converting biomass into useful energy, presented in this paper, are only a small clipping of solutions available on market. However, depletion of them was not the purpose of authors, but presenting the most important, technologically advanced processes, together in one manuscript, which helps to systematize current knowledge on this theme. Because of editorial limitations, we could not manage significant themes such as SunDiesel [21], fuel cells (FC) [22], ORC [23] and other.



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Abstrakt: Wykorzystanie biomasy do produkcji ciepła w procesach bezpośredniego spalania lub współspalania z węglem, polegające na konwersji zawartej w niej energii chemicznej związków węgla, wodoru i tlenu w energię cieplną w kotłach, jest najtańszym, lecz - zdaniem wielu ekspertów - najmniej efektywnym i ekonomicznie



najmniej opłacalnym rozwiązaniem. W przypadku łącznej produkcji energii cieplnej i elektrycznej w elektrociepłowniach opalanych biomasą (drewnem, słomą, surowcem z plantacji energetycznych, RDF-em itd.) nakłady inwestycyjne są trochę wyższe, ale dzięki spalaniu fluidyzacyjnemu, kogeneracyjnym układom skojarzonym, trigeneracji, układom ORC itd. sprawność konwersji rośnie, a także poprawia się efekt ekonomiczny i ekologiczny. Najkorzystniejszą jednak zarówno z punktu widzenia ekonomicznego, jak i technicznego metodą przetworzenia biomasy jest jej częściowe utlenienie, zgazowanie i piroliza, pod kątem produkcji paliw płynnych, z ewentualnym wykorzystaniem syntezy Fischer-Tropscha, uwodornienia i hydrokrakingu w odniesieniu do produktów termicznego rozkładu biomasy. Niniejszy artykuł zawiera przegląd obecnie stosowanych, nowoczesnych technologii wykorzystujących te procesy do produkcji biopaliw gazowych, ciekłych i stałych.

Słowa kluczowe: konwersja biomasy, piroliza, paliwa