SUSTAINABLE
CHEMICAL PROCESSES

REVIEW　　　　　　　　　　　　　　　　　　　　　　**Open Access**

Thermochemical processes for biofuels production from biomass

Nicholas Canabarro, Juliana F Soares, Chayene G Anchieta, Camila S Kelling and Marcio A Mazutti[*]

Abstract

The contribution of biomass to the world's energy supply is presently estimated to be around 10% to 14%. The conversion of biomass to biofuels can be achieved primarily via biochemical and thermochemical processes. Recently, the use of thermochemical processes as pyrolysis and gasification has received great attention. The biomass composition and form of process conduction can affect greatly the efficiency of conversion for both gasification and pyrolysis. This review compiles recent thermochemical studies using several kinds of biomass to obtain biofuels and, additionally, it presents a brief description of main gasification and pyrolysis processes employed. Publications in Patent database also were reported and compiled.

Keywords: Gasification, Pyrolysis, Biofuels, Biomass, Thermochemical processes

Introduction

Recently there has been a renewed interest in using biomass as an energy source due to the increasing demand in global energy coupled with environmental concerns of using fossil fuels. The contribution of biomass to the world's energy supply is presently estimated to be around 10% to 14% [1]. The conversion of biomass to biofuels can be achieved primarily via biochemical and thermochemical processes. The thermochemical processes can convert both food and nonfood biomass to fuel products via pyrolysis and gasification [2]. Thermochemical gasification is a promising technology that can exploit the embedded energy in various types of biomass and convert to valuable products suitable for different industrial applications. Common feedstock for gasification includes agricultural crop residues, forest residues, energy crops, organic municipal wastes, and animal waste [2,3].

Pyrolysis, like gasification, is an advanced thermal treatment that converts a material into a syngas but at lower temperatures and in the absence of oxygen. It is always also the first step in combustion and gasification processes where it is followed by total or partial oxidation of the primary products [4,5]. Despite the calorific value of a gas derived from pyrolysis being higher than that of gasification, the volume of gas produced is usually much lower due to the lack of the oxygen carrier [6-8].

Both pyrolysis and gasification of biomass are complex processes and depends on several factors such as the composition of lignocellulosic material, heating rate and content of inorganic material etc. The amounts of cellulose, hemicellulose and lignin present in the biomass affect the pyrolysis and gasification, implying in great variation in the efficiency among different biomass and process employed. In this sense, the objective of this review is to compile the main biomass used in thermochemical studies. In addition, it will be presented a brief description of main gasification and pyrolysis processes employed as well as the main technologies cited in patent database.

Gasification

In the gasification process, biomass is converted into a syngas by the partial oxidation of biomass at high temperatures [9]. Gasification takes place at moderately high temperature and turns solid biomass into combustible gas mixtures (known as synthesis gas or syngas) through simultaneous occurrence of exothermic oxidation and endothermic pyrolysis under limited oxygen supply [2,10]. The main components of this gas are CO, H_2, CO_2, CH_4, H_2O and N_2. However a variety of tars are also produced during the gasification reaction [11,12]. The resulting syngas can be burned to produce heat or synthesized to produce liquid transportation fuels [2,13]. Figure 1 shows a

* Correspondence: mazutti@ufsm.br
Department of Chemical Engineering, Federal University of Santa Maria, Av. Roraima, 1000, Santa Maria 97105-900, Brazil
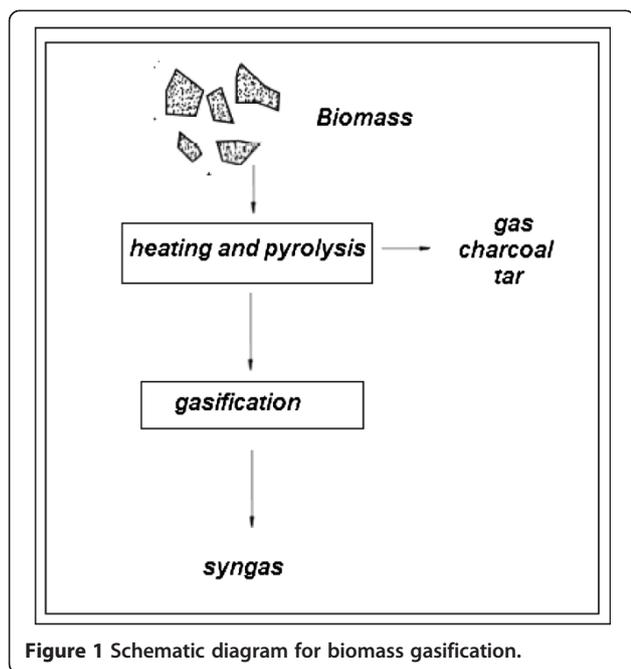
Figure 1 Schematic diagram for biomass gasification.

schematic diagram whose illustrate the biomass gasification technology. Pyrolysis is the first step to occur the gasification.

For the synthesis of liquid fuels and other chemicals only a nitrogen-free syngas is suitable. Several studies on nitrogen conversion in different gasification processes are available in the literature. Fixed bed and fluidized bed gasification are more common. Different gasification agents can be applied, as air, oxygen or steam [14,15].

The use of air as a gasifying agent is most common in industry but yields low heating value gas (4–7 MJ/Nm^3) that is only suitable for heat and power applications. On the other hand, steam and oxygen can increase the heating value of syngas (10–18 MJ/Nm3) and the H_2/CO ratio. A high H_2/CO ratio is required for producing liquid fuels through Fischer–Tropsch synthesis and also benefits the production of H_2 for use in fuel cells. However, high capital costs and complex system design have hindered the applications of steam and oxygen gasification at a large industrial scale [2,16].

There are different gasification processes available in the literature to produce the syngas. The most important methods are described below and, the most significant studies referring gasification of biomass are compiled in Table 1.

Fluidized-bed gasification
In fluidized bed gasifiers, biomass particles are transformed into a fluid-like state through suspension in a gasifying agent, which offer the advantage of a uniform temperature distribution and better solid-gas contact and heat transfer rates. Compared with coal, biomass has lower particle

density, which results in bubble coalescence within the bed and in turn a poor fluidization quality. Therefore, some inert particles (such as silica sand) are added as lubricants to facilitate the fluidization of biomass particles, or natural/artificial catalysts (such as dolomite, olivine, alkali-based catalyst, and metal-based catalyst). These particulates are introduced to improve fluidization quality and to reduce tars in the downstream process. Moreover, these gasifiers are usually equipped with cyclones to remove relatively fine particulates from the raw product gas. Depending on the fluidization pattern and combination character, these gasifiers can be further classified as bubbling fluidized bed, circulating fluidized bed, as showed in Figure 2, and double fluidized bed system. Fluidized bed gasifiers typically operate at temperatures of 800–1000°C to prevent ash from building up. Another advantage of this type of gasifier is that its high thermal inertia and vigorous mixing enables it to gasify different types of fuel, e.g. different types of biomass. This is therefore one of the preferred technologies for large-scale biomass gasification plants [10,17,22,28,29].

Dual fluidized bed gasification (DFB)
The DFB gasifier consists of two reactors, where gasification and combustion take place separately [14]. Circulating bed material between these two reactors carries the heat from the combustion reactor to the gasification reactor [17]. In the DFB gasifier, biomass is gasified with steam. Due to steam gasification, there is virtually no nitrogen in the producer gas and the hydrogen content amounts to about 40%. The average heating value is around 12–14 MJ/Nm^3 (Nm^3 = at 273.15 K and 101.325 Pa, referred to as dry gas). Producer gas from steam gasification is well suitable not only for heat and electricity production, but also for chemical synthesis [14].

Fixed bed gasification
The fluidized bed (FB) provides high mixing and reaction rates, accommodates variation in fuel quality and allows scaling-up of the process. Various concepts have been developed for gasification in FB [31]. In fixed-bed gasifiers, the gas passes through the raw material while the gasifier zones are in "fixed" position where the reactions take place. Depending on the direction of gas flow, these gasifiers can be further classified as updraft, downdraft and cross-flow fixed beds showed in Figure 3 [22].

Supercritical water gasification (SCWG)
This process has the potential to convert biomass with water contents up to 80% directly without the need for an energy-expensive drying step [20]. An advantage of processing wet biomass hydrothermally, rather than drying it, is that doing so avoids the energy penalty

Table 1 Comparison of different types of biomass and gasification process

Process	Biomass	Experimental conditions	Results	Reference
Dual fluidized bed gasifier	Lignite	Input fuel power: 90 kW$_{th}$; Particle size: 370 and 510 μm;	A lower amount of steam and the high catalytic activity of the lignite caused a better performance of the gasification reactor.	[17]
		Steam-to-carbon ratio: 1.3 and 2.1 Kg$_{H2O}$/Kg$_{carbon}$.	The reduction of particle size increases product gas yield in +15.7%.	
	Waste wood; Bark; Plastic residues	Input fuel power: 100 kW; Nitrogen content: 0.05 to 2.70 wt.-%. Temperature: 850°C	The DFB gasifier is suitable for the conversion of fuels with higher loads of nitrogen.	[14]
		Water: 6.1 wt.-% (waste wood); 11.9 wt.-% (Bark)		
	Empty fruit bunches	Moisture: more than 50 wt.%;	The gasification efficiency decreases as the moisture content increases.	[18]
		Particle size: less than 1.0 mm;	A high content of moisture and oxygen resulted in a low calorific value.	
Fluidized bed gasifier	Pine, maple-oak mixture, and discarded seed corn	Gasifying agent: Oxygen and steam	The gasification is most effective for feedstock with low nitrogen and moisture contents.	[2]
		Temperature: 800°C.		
		Input fuel power: 800 kW		
Supercritical water gasification	Indole	Reaction times: 3 –80 min	The yield of CH$_4$ increased significantly as the indole concentration increased.	[19]
		Temperature: 550 and 700°C		
		Initial indole concentration: 0.2 mol/L	Hydrogen and carbon gasification efficiencies exhibited values up to 79% and 20%, respectively.	
		Pressure: 30 MPa		
	Glycerol	Temperature: 300 - 430°C.	The highest rate of coke formation occurred in the temperature range of 350 –370°C, and long residence times.	[20]
		Residence times: 5–120 min.		
		Feed concentrations: 10, 20 e 30 wt.%		
		Pressure: 30 MPa.		
Steam gasification	Sugarcane bagasse	Temperature: 800, 900 and 1000°C;	The increase in reactor temperature resulted in an increase in energy yield and apparent thermal efficiency.	[21]
		Gasifying agent: 8 g/min of steam;		
		Tracer gas: 2.33 g/min of nitrogen;	The enhancement in syngas quality at the 1000°C case resulted in an increase of energy yield.	
		Sample: 15 g of sugarcane bagasse.		
	Biomass not specified.	Temperature: 800°C to 1200°C.	Higher gasification temperature leads to higher energy efficiencies of product gas and lower energy efficiencies of tar.	[22]
Entrained-flow gasifier	Raw bamboo; Torrefied bamboo; High-volatile bituminous coal	Gasification agent: Oxygen;	The carbon conversions of the three fuels are higher than 90%.	[23]
		Sizes of the particles: 44 – 250 μm;		
		fuel temperature: 300 K;		
		Pressure: 2 Mpa.		
Atmospheric pressure gasifier and the pressurized gasifier.	Forest residue	Moisture: 10 – 20%;	In comparison with fuels and chemicals from conventional feedstocks, biomass based fuels and chemicals are expensive.	[24]
		Feedstock size: 20 – 80 mm.		
Fixed bed reactor	Crude glycerol with olive kernel	Temperature: 750–850°C	H$_2$ concentration increased from 19 to 33% (v/v) and the tar yield decreased from 19.5 to 2.4 wt% at conditions of T = 850°C and λ = 0.4.	[25]
		Air ratios of λ = 0.2–0.4		
	Pine; Red oak; Horse manure; Cardboard	Temperature: 800°C;	The thermodynamic efficiencies for the gasifier were found in the range of 81.7–84.6%	[26]
		Moisture: 12.2 wt.% (Pine), 14.8 wt.% (Red oak) 18.33 wt.% (Horse manure) 12.6 wt.% (Cardboard)		

Table 1 Comparison of different types of biomass and gasification process (Continued)

Packed-bed reactor.	Mixture of polypropylene and poplar sawdust	Temperature: 400 to 800°C; Particle size: 2 mm (sawdust); 3 mm (polypropylene)	The increase of temperature led to the decrease of the solid residues fraction and an increase in the gas yield.	[27]
			Optimum temperature: 700°C	

associated with the phase change of the water. This leads to an improvement in economic performance compared with a conventional gasification process [19]. These systems make use of the conditions of the critical point of water at 647.3 K and a pressure of 22.1 MPa as a favorable environment for wet biomass gasification reactions [29].

Plasma gasification

Plasma is considered to be the fourth state of matter, consisting of a mixture of electrons, ions and neutral particles, although overall it is electrically neutral. The degree of ionization of a plasma is the proportion of atoms that have lost (or gained) electrons. Plasma technology involves the creation of a sustained electrical arc by the passage of electric current through a gas in a process referred to as electrical breakdown. Because of the electrical resistivity across the system, significant heat is generated, which strips away electrons from the gas molecules resulting in an ionized gas stream, or plasma [15,34]. Plasma gasification processes may reach temperatures from 2,000 to 30,000°C [29].

A general analysis of data compiled in Table 1 reveals that fluidized and fixed-bed reactors are more usual in gasification procedures. The variable more studied is temperature, where it is seen that at high temperature the energy production and the syngas quality increases,

beyond that decrease the tars production. The particle size and the moisture have a significant influence in the gasification process, but if the particle size is reduced the syngas production increases and at high moisture contents the efficiency of gasification decrease.
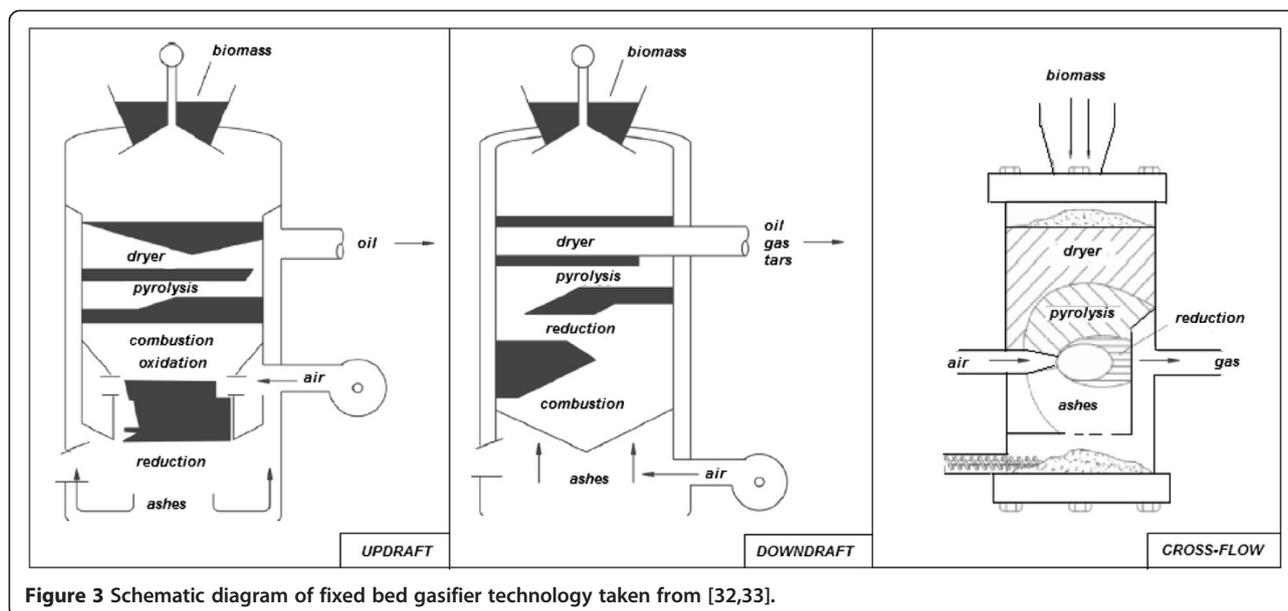
Pyrolysis

Pyrolysis is an advanced thermal treatment that converts a material into a syngas at temperatures around 1000°C and in the absence of oxygen. Pyrolysis also can be described as the direct thermal decomposition of the organic matrix that could obtain solid, liquid and gas products [35-37]. Temperature is the most important factor for the product distribution of pyrolysis, most interesting range for the production of the pyrolysis products is between 625 and 775 K. The charcoal yield decreases as the temperature increases. Yield of products resulting from biomass pyrolysis can be maximized as follows: charcoal (a low temperature, low heating rate process), liquid products (a low temperature, high heating rate, short gas residence time process), and fuel gas (a high temperature, low heating rate, long gas residence time process) [8,38,39].

Lower process temperature and longer vapour residence times favour the production of charcoal. High temperature and longer residence time increase the biomass conversion
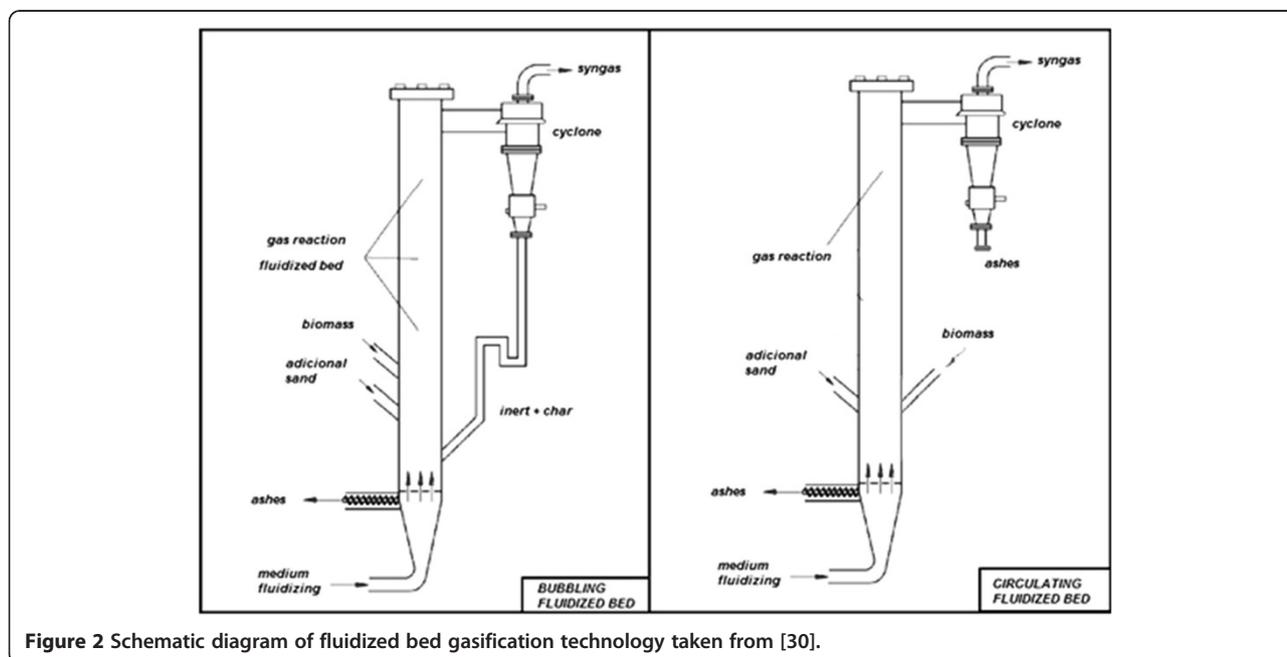
Figure 2 Schematic diagram of fluidized bed gasification technology taken from [30].

Figure 3 Schematic diagram of fixed bed gasifier technology taken from [32,33].

to gas and moderate temperature and short vapour residence time are optimum for producing liquids [4,40]. Short residence time pyrolysis of biomass at moderate temperatures has generally been used to obtain high yield of liquid products. For highly cellulosic biomass feedstocks, the liquid fraction usually contains acids, alcohols, aldehydes, ketones, esters, heterocyclic derivatives and phenolic compounds [35,41,42].

The pyrolysis process for fuels and chemicals could be divided in: catalytic, fast and flash. The difference between them are the process conditions which involves the solid residence times, heating rate, particle size and temperature. These can be used for a commercial production of a wide range of fuels and chemical from biomass feedstocks [38,43,44]. To produce these syngas four different methods are applied, which are discussed below. A compilation among of different types of biomass and pyrolysis processes is described in Table 2.

Slow pyrolysis
Biomass is pyrolysed at slow heating rates (5–7 K/min). This leads to less liquid and gaseous product and more of char production, at low temperature (675–775 K), and/or gas, at high temperature. Significant amount of work has been done on this process. The most used reactors in this process are fixed bed and tubular reactor [9].

Fast pyrolysis
Fast pyrolysis is a process in which a material, such as biomass, is rapidly heated to high temperatures in the absence of air (specifically oxygen). It involves fast heating of biomass but not as fast as flash pyrolysis. Heating rate is

somewhere about 300°C/min. Generally, fast pyrolysis is used to obtain high-grade bio-oil. Fast pyrolysis is successful with different reactors configurations, some of them are fluidized-bed reactors, entrained flow reactor, wire mesh reactor, vacuum furnace reactor, vortex reactor, rotating reactor, circulating fluidized bed reactor. If the purpose was to maximize the yield of liquid products resulting from biomass pyrolysis, a low temperature, high heating rate, short gas residence time process would be required. If the purpose were to maximize the yield of fuel gas resulting from biomass pyrolysis, a high temperature, low heating rate, long gas residence time process would be preferred [9,53-55].

Flash pyrolysis
Flash pyrolysis is the process in which the reaction time is of only several seconds or even less. The heating rate is very high. This requires special reactor configuration in which biomass residence times are only of few seconds. Two of appropriate designs are entrained flow reactor and the fluidized-bed reactor. Flash pyrolysis of any kind of biomass requires rapid heating and therefore the particle size should be fairly small. Major problem of the present reactors for flash pyrolysis are the quality and the stability of the produced oil, strongly affected by char/ash content of bio-oil. Besides the known problems concerning solid particles in the bio-oil, char fines will catalyze repolymerization reactions inside the oil resulting in a higher viscosity. Flash pyrolysis is of following types: flash hydro-pyrolysis is flash pyrolysis done in hydrogen atmosphere, it is carried out at a pressure up to 20Mpa; rapid thermal process is a particular heat transfer process with very short heat residence times

Table 2 Comparison of different types of biomass and pyrolysis process

Process	Biomass	Experimental conditions	Results			Reference
	Wood	Moderate temperature, short residence time vapour	Char%	Liquid%	Gas%	[4,45-47]
			12	75	13	
	Lignocellulosic	Fluid Bed 500℃	41,67% C 7,87% H 50,46% O			
	Beech					
	Miscanthus		43,13% C 8,14% H 0,22% N 48,51% O			
	Spruce		43,66% C 7,67% H			
			48,67% O			
Fast	Beech	Circulation Fluidised	39,45% C 7,96% H 0,001% N 52,58% O			
	Forest residue	Bed	39,44% C 8,01% H 0,30% N 52,25% O			
		500℃				
	Pine	Ablative 480℃	41,27% C 7,79% H			
			0,01% N 50,93% O			
		Ablative 560℃	32,64% C 8,01% H			
			0,35% N 58,31% O			
	Eugenol	Non-isothermal laminar-flow	Phenol, furans, ethers, acids, single-ringaromatic			
		300-900℃				
		Atmospheric pressure				
		Residence times 1–3 s				
	Raw-straw	Fluidized Bed	C-Biooil wt%	E- Biooil wt%	Gases%	
		350℃	32,59	13,96	30,6	
		500℃	23,48	6,08	49,3	
	HF-straw	350℃	29,34	26,04	28,2	
		500℃	21,59	13,56	57,1	
Slow	Spruce	Fixed Bed	22.56% C 10,8% H 0,3% N 63,34% O			[45]
		500℃				
Flash	Celulose, sugar cane bagasse	Fixed Bed with H_2	10-20% O			[35]
		Hidropyrolysis 10 Mpa				
	Oil palm shell	Fluidised Bed with N_2	High fraction of phenol			
	Pine and spruce	550℃	Oxygenated organic compounds aldehydes, acids, ketones and metoxylated phenols			
	Wood	Fluidised Bed	Liquids homogeneous			
		400-550℃	Phenolic compounds			
		Free Fall	Aromatic compounds			
		Atmospheric pressure				
		700-900℃				
		Circulating Fluidised Bed	Non-hidrocarbons and alkanes-aromatics			
	Rape seed grains	Fluidised Bed,	Fatty acids			
		500-600℃				
	Wood chips and rice shell	Powder-particle; Catalitic; Fluidised Bed 427℃	Aromatic hydrocarbons			
	Birch bark, birch sapwood	One step and stepwise	Phenols			
		Vacuum 275-350℃				
NE	Grape	Tubular Batch with N_2	43,21% C 5,94% H			[9,48-50]
		40-50℃/min	45,50% O 0,65% N 1,24% S			

Table 2 Comparison of different types of biomass and pyrolysis process (Continued)

Neem Seed	Semi-batch 400-500℃ 20℃/min	38% oil, large pore size, high clorific value			
Palm seed	200-450℃	45,3% C, 5,6% H, 1% N, 0,8% S, 47,2% O			
Palm leaf		49,4% C, 5,8% H, 1,3% N 1,3% S, 42,3% O			
Palm leaf stem		36,1% C, 5,2% H, 0,7% N, 0,7% S, 57,2% O			
Palm bituminous coal		73,1% C, 5,5% H, 1,4% N, 1,7% S, 8,7% O			
Wood	400℃	Char%	Liquid%	Gases%	
		24,1	65,5	10,2	
	450℃	21,4	65,7	11,1	
	500℃	18,9	66	14,6	
	550℃	17,3	67	14,9	
	550℃	16,7	67,8	15,7	
	550℃	17,1	66,2	15,2	
Esparto grass	Oxidative pyrolysis inert atmosphere 25-650℃	0,50% N, 38,16% C, 5,40% H, 55,94% O			
Straw		0,21% N, 42,93% C, 6,16% H, 50,70% O			[51]
Posidonea Oceanic seaweed		0,71% N, 34,85% C, 4,54% H, 0,62% S, 59,28% O			
agricultural urban pruning waste		2,09% N, 48,06% C, 5,81% H, 44,04% O			
waste of forest pruning		0,65% N, 40,12% C, 5,44% H, 53,79% O			
Xylan	Steam pyrolysis; 5×10^5 Pa	Char%	Liquid%	Gases%	[52]
	703℃	29,7	53,3	16,9	
	873℃	22,4	53,2	24,4	
Celulose	703℃	21	70,4	8,6	
	873℃	17,5	68,7	13,8	
Lignin	703℃	55,9	40,4	3,7	
	873℃	48,5	40	11,5	

(between 30 ms and 1.5 s). It is done at temperatures between 400 and 950 1C; rapid de-polymerization and cracking of feed stocks takes place; rapid heating eliminates the side reactions whereby giving products with comparable viscosity to diesel oil; solar flash pyrolysis concentrated solar radiation can be used to perform flash pyrolysis; vacuum flash pyrolysis the process is done under vacuum, the vacuum facilitates the removal of the condensable products from the hot reaction zone [56-58].

Catalytic biomass pyrolysis

From literature it was seen that liquids obtained from biomass by slow, flash or fast pyrolysis process, could not be directly used as transportation fuel. This oil needs to be upgraded as they have high oxygen and water content. These oils are also found to be less stable and less miscible in conventional fuels. Catalytic biomass pyrolysis is introduced to improve the quality of the oil produced [38,59,60].

Table 3 Recent technologies in gasification and pyrolysis process

	Process	Patent	Registration number	Reference
Gasification	Gas/shaft process	Method and apparatus for coproduction of pig iron and high quality syngas.	WO 2012/018394 A3	[65]
	N.E.	Nanoparticle catalyst and method of using the same for biomass gasification.	US 2011/0315931 A1	[66]
	Fischer-Tropsch reactor	Method of puryfing a gas.	US 2012/0202897 A1	[67]
	Fluidized bed gasifier	Pretreatment of biomass feed for gasification.	US 2012/0266531 A1	[61]
	Mixed flow	Method and device for mixed flow type gasification of biomass.	US 2012/159469 A1	[68]
	Fluidized bed and downstream edge	Method for producing production gas and apparatus using same.	US 2012/176611 A1	[62]
	N.E.	Ammonia production by integrated intencified process.	WO 2012/025767 A3	[69]
	Combined reactor	A processes and a system for the gasification and/or combustion of biomass and/or coal with and at least partial carbon dioxide separation.	WO 2012/103997 A1	[70]
Pyrolysis	NE	Production of stable biomass pyrolysis oils using fractional catalytic pyrolysis	US 2010/0212215 A1	[71]
	Producing of biofuel by fast pyrolysis of organic material, using a system of three interconnected serial fluidized bed reactors	Equipment and a method for generating biofuel based on rapid pyrolysis biomass	US 2011/0219680 A1	[72]
	Producing substitute natural gas (hydrocarbons) from forestry residues by hydropyrolysis	Sorption enhanced methanation of biomass	US 2013/0017460 A1	[73]
	NE	Method and apparatus for pyrolysis and gasification of biomass	US 2013/0125465 A1	[74]
	Reactor with rotational chamber for pyrolysis of biomass to conversion in energy	Reactor for pyrolysis of biomass	WO 2011/034409 A1	[75]
	NE	Process for catalytic hydrotratament of a pyrolysis oil	WO 2011/064172 A1	[63]
	Pyrolytic conversion of biomass materials into stable fuels and other usable products	Production of pyrolysis oil	WO 2011/103313 A2	[76]
	Effective pyrolysis of a biomass utilizing rapid heat transfer from a solid heat carrier or catalyst	Method and apparatus for pyrolysis of a biomass	WO 2012/012191 A1	[64]

Technologies

Table 3 shows the latest technologies that involves the production of syngas and biofuels by gasification and pyrolysis processes from biomass. The gasification process by fluidized-bed reactor is the most common among registered technologies, as showed in Table 3. The registered patents, US 2012/0266531 A1 [61] e US 2012/176611 A1 [62], use this process to make a pretreatment of biomass and to produce the syngas. Referring the technologies for pyrolysis, it is found registers for catalitic pyrolysis, fast pyrolysis e hidropyrolysis. Catalitic pyrolysis is the most used technology, where the registered patents WO 2011/064172 A1 [63] used catalysts to make an oil, whereas WO 2012/012191 A1 [64] used the effective pyrolysis of biomass to produce biofuels through fast thermal exchange.

Competing interests
The authors declare that they have no competing interests.

Authors' contributions
All authors contributed equally in this work. All authors read and approved the final manuscript.

References
1. Shen Y, Yoshikawa K: **Recent progresses in catalytic tar elimination during biomass gasification or pyrolysis: a review.** *Renew Sustain Energy Rev* 2013, **21**:371–392.
2. Huynh CV, Kong S: **Performance characteristics of a pilot-scale biomass gasifier using oxygen-enriched air and steam.** *Fuel* 2013, **103**:987–996.
3. Higman C, van der Burgt M: *Gasification*, Elsevier science. 2dth edition. Burlington, MA, USA: Gulf Professional Publishing; 2003.
4. Bridgwater AV: **Renewable fuels and chemicals by thermal processing of biomass.** *Chem Eng J* 2003, **91**:87–102.
5. Yang J, Blanchette D, De CB, Roy C: **Modelling, scale-up and demonstration of a vacuum pyrolysis reactor.** In *Thermochemical biomass conversion*, Volume 107. Edited by Bridgwater AV. Oxford, UK: Blackwell Scientific Publications; 2001:1296–1311.

6. Lupa CJ, Wylie SR, Shaw A, Al-Shamma'a A, Sweetman AJ, Herbert BMJ: Experimental analysis of biomass pyrolysis using microwave-induced plasma. *Fuel Process Technol* 2012, **97**:79–84.
7. Neves D, Thunmanb H, Matos A, Tarelhoa L, Gómez-Bareac A: Characterization and prediction of biomass pyrolysis products. *Progress Energy Combustion Sci-ence* 2011, **37**:611–630.
8. Mohan D, Pittman CU Jr, Steele PH: Pyrolysis of wood/biomass for bio-oil: acritical review. *J Energy Fuels* 2006, **20**:848–889.
9. Goyal HB, Seal D, Saxena RC: Bio-fuels from thermochemical conversion of renewable resources: a review. *Renew Sustain Energy Rev* 2008, **12**:504–517.
10. Basu P: *Biomass gasification and pyrolysis: practical design and theory.* 1st edition. Burlington, USA: Elsevier Inc; 2010.
11. Hindsgaul C, Schramm J, Gratz L, Henriksen U, Dall Bentzen J: Physical and chemical characterization of particles in producer gas from wood chips. *Bioresour Technol* 2000, **73**:147–155.
12. Barman NS, Ghosh S: Gasification of biomass in a fixed bed downdraft gasifier: a realistic model including tar. *Bioresour Technol* 2012, **107**:505–511.
13. Brown RC: Biorenewable resources: engineering new products from agriculture. *Iowa State Press* 2003.
14. Wilk V, Hofbauer H: Conversion of fuel nitrogen in a dual fluidized bed steam gasifier. *Fuel* 2013, **106**:793–801.
15. Kalinci Y, Hepbasli A, Dincer I: Exergoeconomic analysis and performance assessment of hydrogen and power production using different gasification systems. *Fuel* 2012, **102**:187–198.
16. Swanson R, Platon A, Satrio J, Brown RC: Techno-economic analysis of biomass-to-liquids production based on gasification. *Fuel* 2010, **89**:11–19.
17. Kern S, Pfeifer C, Hofbauer H: Gasification of lignite in a dual fluidized bed gasifier: Influence of bed material particle size and the amount of steam. *Fuel Process Technol* 2013, **111**:1–13.
18. Mohammed MAA, Salmiaton A, Azlina WAKG W, Amran MSM: Gasification of oil palm empty fruit bunches: a characterization and kinetic study. *Bioresour Technol* 2012, **110**:628–636.
19. Guo Y, Wang S, Huelsman CM, Savage PE: Products, pathways, and kinetics for reactions of indole under supercritical water gasification conditions. *J Supercrit Fluids* 2013, **73**:161–170.
20. Müller JB, Vogel F: Tar and coke formation during hydrothermal processing of glycerol and glucose. Influence of temperature, residence time and feed concentration. *J Supercrit Fluids* 2012, **70**:126–136.
21. Ahmed II, Gupta AK: Sugarcane bagasse gasification: global reaction mechanism of syngas evolution. *Appl Energy* 2012, **91**:75–81.
22. Zhang Y, Li B, Li H, Zhang B: Exergy analysis of biomass utilization via steam gasification and partial oxidation. *Thermochim Acta* 2012, **538**:21–28.
23. Chen W, Chen C, Hung C, Shen C, Hsu H: A comparison of gasification phenomena among raw biomass, torrefied biomass and coal in an entrained-flow reactor. *Appl Energy* 2013, **xxx**:xxx.
24. Sarkar S, Kumar A, Sultana A: Biofuels and biochemicals production from forest biomass in western Canada. *Energy* 2011, **36**:6251–6262.
25. Skoulou VK, Zabaniotou AA: Co-gasification of crude glycerol with lignocellulosic biomass for enhanced syngas production. *J Anal Appl Pyrolysis* 2013, **99**:110–116.
26. Lee U, Balu E, Chung JN: An experimental evaluation of an integrated biomass gasification and power generation system for distributed power applications. *Appl Energy* 2013, **101**:699–708.
27. MENG Q, Chen X, Zhuang Y, Liang C: Effect of temperature on controlled air oxidation of plastic and biomass in a packed-bed reactor. *Chem Eng Technol* 2013, **36**(2):220–227.
28. Rapagna S, Jand N, Kiennemann A, Foscolo PU: Steam-gasification of biomass in a fluidized-bed of olivine particles. *Biomass Bioenergy* 2000, **19**:187–197.
29. Ruiz JA: Biomass gasification for electricity generation: review of current technology barriers. *Renew Sustain Energy Rev* 2013, **18**:174–183.
30. Olofsson I, Nordin A, Sönderlimd U: *Initial Review and Evaluation of Process Technologies and Systems Suitable for Cost-Efficient Medium-Scale Gasification for Biomass to Liquid Fuels.* 2005. ISSN 1653-0551 ETPC Report 05-02, Energy Technology & Thermal Process Chemistry, University of Umeå, Sweden.
31. Gómez-Barea A, Ollero P, Leckner B: Optimization of char and tar conversion in fluidized bed biomass gasifiers. *Fuel* 2013, **103**:42–52.
32. Mckendry P: Energy production from biomass (part 3): GasificationTechnologies. *Bioresour Technol* 2002, **83**(1):55–63.
33. Battacharya SC, Siddique AH, Pham HL: A study on wood gasification for Low-Tar Gas production. *Energy* 1999, **24**:285–296.
34. Gomez E, Rani DA, Cheeseman CR, Deegan D, Wise M, Boccaccini AR: Thermal plasma technology for the treatment of wastes: a critical review. *J Hazard Mater* 2009, **161**:614–626.
35. Yaman S: Pyrolysis of biomass to produce fuels and chemical feedstocks. *Energy Convers Manag* 2004, **45**:651–671.
36. Raveendran K, Ganesh A: Flash pyrolysis of sunflower oil cake for production of liquid fuels. *Fuel* 1996, **75**:1715–1720.
37. MEIER D, FAIX O: State of the art of applied fast pyrolysis of lignocellulosic materials—a review. *Biosource Technol* 1999, **68**(1):71–77.
38. Balat M, Balat M, Kirtay E, Balat H: Main routes for the thermo-conversion of biomass into fuels and chemicals. Part 1: pyrolysis systems. *Energy Convers Manag* 2009, **50**:3147–3157.
39. Abella L, Nanbu S, Fukuda K: A theoretical study on levoglucosan pyrolysis reactions yielding aldehydes and a ketone in biomass. *Mem Fac Eng, Kyushu Univ* 2007, **67**:67–74.
40. Diebold JP: A review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-oils. In *Fast pyrolysis of biomass: a handbook*, Volume 2. Edited by Bridgwater AV. Newbury, UK: CPL Press; 2002:243–292.
41. Gullu D, Demirbas A: Biomass to methanol via pyrolysis process. *Energy Conv Manage* 2001, **42**:1349–1356.
42. Fisher T, Hajaligol M, Waymack B, Kellogg D: Pyrolysis behavior and kinetics of biomass derived materials. *J Anal Appl Pyrol* 2002, **62**:331–349.
43. Zhang O, Chang J, Wang T, Xu Y: Review of biomass pyrolysis oil properties and upgrading research. *Energy Convers Manage* 2007, **48**:87–92.
44. Bakis R: Alternative electricity generation opportunities. *Energy Source Part A* 2008, **30**:141–148.
45. Blin J, Volle G, Girard P, Bridgwater T, Meier D: Biodegrability of biomass pyrolysis oils: comparison to conventional petroleum fuels and alternatives fuels in current use. *Fuel* 2007, **86**:2679–2686.
46. Ledesma EB, Campos C, Cranmer DJ, Foytik BL, Ton MN, Dixon EA, Chirino C, Batamo S, Roy P: Vapour –phase cracking of eugenol: distribuition of tar products as fuctions of temperature and residence time. *Energy and Fuels* 2013, **27**:868–878.
47. Eom I, Kim J, Lee S, Cho T, Yeo H, Choi J: Comparison of pyrolytic products produced from inorganic-rich and demineralized rice straw (oryza sativa L.) by fluidized bed pyrolyzer for future biorefinery approach. *Bioresour Technol* 2013, **128**:664–672.
48. Marculescu C, Ciuta S: Wine industry waste termal processing for derived fuel properties improvement. *Renew Energy* 2013, **57**:645–652.
49. Nayan NK, Kumar S, Singh RK: Production of the liquid fuel by thermal pyrolysis of neem seed. *Fuel* 2013, **103**:437–443.
50. Sait HH, Hussuain A, Salema AA, Ani FN: Pyrolysis and combustion kinetics of date palm biomass using thermogravimetric analysis. *Bioresour Technol* 2012, **118**:382–389.
51. Conesa JA, Domene A: Biomasses pyrolysis and combustion kinetics through n-th order parallel reactions. *Thermochimical Acta* 2011, **523**:116–181.
52. Giudicianni P, Cardone G, Ragucci R: Cellulose, hemicellulose and lignin slow steam pyrolysis: thermal decomposition of biomass components mixtures. *J Anal Apllied Pyrolysis* 2013:213–222.
53. Luo Z, Wang S, Liao Y, Zhou J, Gu Y, Cen K: Research on biomass fast pyrolysis for liquid fuel. *Biomass Bioenergy* 2004, **26**:455–462.
54. Onay O, Beis SH, Kockar OM: Fast pyrolysis of rape seed in well-swept fixed bed reactor. *J Anal Appl Pyrolysis* 2001, **58–59**:995–1007.
55. Onay O, Kockar OM: Technical note: slow, fast and flash pyrolysis of rape seed. *Renew Energy* 2003, **28**:2417–2433.
56. Gercel HF: Production and characterization of pyrolysis liquids from sunflower pressed bagasse. *Bioresource Technol* 2002, **85**:113–117.
57. Funino J, Yamaji K, Yamameto H: Biomass-balance table for evaluating bioenergy resources. *Appl Energy* 1999, **63**:75–89.
58. Lede J, Bouton O: Flash pyrolysis of biomass submitted to a concentrated radiation. Application to the study of the primary steps of cellulose thermal decomposition. In *Division of fuel chemistry; reprints of symposia, vol. 44(2), 217th ACS meeting, 21–25 march*. Anaheim, USA; 1999.
59. Pattiya A, Titiloye JO, Bridgwater AV: Catalytic pyrolysis of cassava rhizome. In *Proceedings of 2nd joint international conference on sustainable energy and environment technology and policy innovations – SEE 2006*. Bangkok, Thailand; 2006.
60. Pattiya A, Titiloye JO, Bridgwater AV: Fast pyrolysis of cassava rhizome in the presence of catalysts. *J Anal Appl Pyrolysis* 2008, **81**:72–79.
61. Hitchingham Jacqueline R, White Lloyd R: *Pretreatment of biomass feed for gasification*. United States Patent Application 2012/0266531 A1; 2012.

62. Shigeru M: *Surface inspection method and surface inspection apparatus.* US United States Patent Application 2012/176611 A1; 2012.

63. Hogendoorn J, Kersten S, Meesala L, De Miguel F: *Process for catalytic hydrotreatment of a pyrolysis oil.* WO Patent Application 2011/064172 A1; 2011.

64. Bartek R, Cordle R: *Method and apparatus for pyrolysis of a biomass.* WO International Patent Application 2012/012191 A1; 2012.

65. Huang X, Hwang J: *Method and apparatus for coproduction of pig iron and high quality syngas.* WO International Patent Application 2012/018394 A3; 2012.

66. Aradi AA, Roos JW, Tze-chi: *Nanoparticle catalysts and method of using the same for biomass gasification.* US United States Patent Application 2011/0315931 A1; 2011.

67. Keskinen Kari I, Koskinen, Jukka, Aittamaa, Juhani, Pettersson, Marianne: *Method of purifying a gas.* US United States Patent Application 2012/0202897 A1; 2012.

68. Xianqi P, Deren S, Chuangzhi W, Xiuli Y, Zhaoqiu Z: *Procédé et dispositif pour la gazéification de type à écoulements mélangés d'une biomasse.* US United States Patent Application 2012/159469 A1; 2012.

69. Sascha AC, Bradford SF: *Method and apparatus for sealing a wellbore.* WO International Patent Application 2012/025767 A3: WO International Patent Application 2012/025767 A3; 2013.

70. Paul S: *Procédé et système pour la gazéification et/ou la combustion de biomasse et/ou de charbon avec une séparation de dioxyde de Carbone au moins partielle.* WO International Patent Application 2012/103997 A1; 2012.

71. Foster AA: *Production of stable biomass pyrolysis oils using fractional catalytic pyrolysis.* United States Patent Application 2010/0212215 A1; 2010.

72. Igor WF: *Equipment and method for generating biofuel based on rapid pyrolysis of biomass.* US United States Patent Application 2011/0219680 A1; 2011.

73. Bowie GK MB, Brian GS, Edson NG: *Sorption enhanced methanation of biomass.* US United States Patent Application 2013/0017460 A1; 2013.

74. Tang H, Zhang Y, Chen Y: *Method and apparatus for pyrolysis and gasification of biomass.* US United States Patent Application 2013/0125465 A1; 2013.

75. Merola R: *Reactor for pyrolysis of biomass.* WO International Patent Application 2011/034409 A1; 2011.

76. Agblevor F: *Production of pyrolysis oil.* WO International Patent Application 2011/103313 A2; 2011.