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A Review of Catalysts Used in Microwave Assisted Pyrolysis and Gasification

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ABSTRACT

The review describes different catalysts and reactor-types used in microwave-assisted thermochemical biomass conversion. We present comparative review of various catalytic experiments and experimental conditions using catalysts in both in situ and ex situ processes. In situ catalytic processes are more frequently used due to simpler experimental set up. However, the process leads to higher catalytic deactivation rate and catalyst recovery is difficult. Catalysts used in ex situ processes require a more complex experimental set-up, the advantage being the fact that optimum temperature can be obtained to achieve best results Catalyst recovery is facile, and its deactivation occurs at a lower rate. The catalysts described herein represent just a small part of the catalyst types/family that can be theoretically used. Commonly used catalysts are zeolites, metal oxides, various salts or carbon type materials but other materials or improvements of those mentioned need to be tested in the future.

Keywords: *in situ* catalysts, *ex situ* catalysts, microwave assisted pyrolysis, microwave assisted gasification

1. Introduction

Due to the high demand for energy worldwide and unreliable fossil fuel prices, significant R&D efforts are focused on other sources of energy. Biofuels derived from lignocellulosic biomass, can overcome most of the limitations posed by first generation biofuel (ethanol and biodiesel) derived from food sources (Naik et al., 2010). Thermochemical and biochemical conversion is a common route for conversion of biomass to desired bioproducts (Sikarwar et al., 2017). The schematic depicts the different types of thermochemical conversion pathways (Sikarwar et al., 2017) (Figure 1). Pyrolysis and gasification offer reliable sources of energy in the form of syngas, bio-oil and biochar from agricultural, forest and municipal waste. Gasification is a thermochemical degradation of biomass to form syngas through series of chemical reactions at high temperatures (700-1100 °C) and controlled oxygen environment. Gasification is performed in the presence of steam or partial air pressure. Combustion reactions are main set of reactions during gasification, however, unlike combustion itself, gasification process uses in general about one third of the oxygen thus only partially oxidizes the carbon rich feedstock, producing less CO_2 and high amounts of CO and H_2 (Basu, 2010) (eq. 1). as given by (Kumar et al., 2009).

CH_xO_y (biomass) + O_2 (21% of air) + H_2O (steam) = $CH_4 + CO + CO_2 + H_2 + H_2O$ (unreacted steam) + C (char) + tar (1)
$C + 1/2O_2 = CO$ (partial oxidation reaction) (2)
$C + O_2 = CO_2$ (complete oxidation reaction) (3)
$C + 2H_2 = CH_4$ (hydrogasification reaction) (4)
$CO + H_2O = CO_2 + H_2$ (water gas shift reaction) (5)
$CH_4 + H_2O = CO + 3H_2$ (steam reforming reaction) (6)
$C + H_2O = CO + H_2$ (water gas reaction) (7)
$C + CO_2 = 2CO$ (Boudourd reaction) (8)

Other secondary reactions are methane reforming and water-gas shift (steam reforming) reactions. The gaseous products obtained is a mixture of H_2, CO, CO_2, CH_4, C_2H_4 and impurities including SO_x, NO_x, condensable HCs (hydrocarbons) and tar.

Pyrolysis is a thermochemical decomposition of biomass to produce liquid fuel in total absence of oxygen (Basu, 2010). Pyrolysis temperature is lower than gasification ranging from 400-700 °C (Demirbas, 2009). The resulting vapors are quenched to form a complex liquid mixture of organic molecules (Demirbas, 2009). The incondensable gases are mainly composed of CO_2, CO and CH_4. The optimum liquid yield depends on multiple factors including pyrolysis temperature and heating rates. A temperature between 500-600 °C and a heating rate of 100 – 1000 °C/s often gives maximum liquid yield (up to 60-70%). The resulting oil can be further processed to produce fuels and other value-added chemicals.

Products from gasification and pyrolysis have certain limitations and cannot be used for application in their current state. These limitations include low heating value, higher oxygen content and higher impurities amongst others. Gasification products have high tar content and other impurities. One way to produce syngas free of tar and methane is by operating gasification at temperatures above 1200 °C but this process can be very energy intensive. Use of catalysts reduces the operating temperature and a suitable catalyst can produce tar free syngas and reform methane to yield high H_2 content. Suitable catalysts can also be used to achieve specific products through Fischer-Tropsch and methanol synthesis reactions. Bio-oil obtained from pyrolysis of biomass has high concentration of oxygenated compounds (Dinesh Mohan, 2006) hence low energy density. The oil is upgraded through a deoxygenation process, resulting in a mixture with high concentration of hydrocarbons. Most common methods to upgrade biofuel is via thermo-catalytic upgrading (Mortensen et al., 2011; Serrano-Ruiz & Dumesic, 2011). Pyrolysis, gasification and upgrading can be performed by conventional or microwave heating, the latter being preferred lately due to its advantages, such as fast heating and short processing time (Fernandez, 2015). Catalytic upgrading is performed either *in situ* or *ex situ*.

Catalysts, play a crucial role in pyrolysis and gasification processes. Main purpose of catalytic pyrolysis is the removal of oxygenated compounds and cracking high molecular weight products to lower chain compounds (Pattiya, 2018). In general, catalytic pyrolysis is accompanied by a multitude of reactions which include cracking, hydrocracking, C-C bonds cleavage, aromatic side-chain scission, isomerisation, polymerisation, hydrogen transfer, dehydration, decarboxylation, decarbonylation, ketonisation, condensation, alkylation, cyclisation, or aromatisation (Pattiya, 2018). The resulting bio-oil have low oxygen content and molecular weight. There are three possible pathways for O_2 removal (Pattiya, 2018): decarbonylation, in the form of CO, decarboxylation as CO_2 and through dehydration, as H_2O. Decarboxylation is most desirable since for one C mole, two moles of O_2 are removed and H_2 is retained.

Depending on the desired products, various types of catalysts are used. Zeolites improve aromatics yield (Fan et al., 2017a; Fan et al., 2017b; Liu et al., 2017), while metal oxides and carbon based catalysts increase syngas production (Dong et al., 2018b; Yu et al., 2014; Zhang et al., 2015b). A catalyst with high surface area and acidity or a microporous catalyst may produce more gases at the expense of the liquid yield (Miandad et al., 2016). On the other hand, a macroporous catalysts may increase the liquid and char yields (Miandad et al., 2016). Zeolites are among the most used types of catalysts. They have many applications and their catalytic activity is related to their shape selectivity and acidity (Pattiya, 2018). ZSM-5 zeolite is an effective deoxygenation catalyst (Pattiya, 2018). Oxygen is removed in the form of CO and CO_2, at high catalyst temperatures and in the form of H_2O at lower temperatures (Pattiya, 2018). The mechanism of reforming and cracking using ZSM-5 is yet to be completely understood. It has been described (Bridgwater, 1994) it as a combination of cracking on the surface of the catalyst followed by the synthesis of aromatics in the zeolite pores. It was proposed (Williams & Horne, 1995) that a dual mechanistic route occurs in the formation of aromatics and polyclinic aromatics when using ZSM-5 as catalyst. In the beginning, low molecular weight hydrocarbons (e.g. alkene gases) forms on the catalyst which then suffer aromatization reactions to produce aromatic compounds. Moreover, deoxygenation reactions may directly form aromatic compounds without taking the alkene route.

Other frequently used catalyst class is metal oxides. They possess either redox properties or acid base properties. Acidic metal oxides (Al_2O_3, SiO_2) deoxygenate pyrolysis vapors by decarbonylation reactions, releasing CO (Pattiya, 2018; Stefanidis et al., 2011), while basic metal oxides (MgO, CaO) reduce the oxygen content in the bio-oil, releasing CO_2 (Pattiya, 2018; Stefanidis et al., 2011). Addition of acidic metal oxides resulted in a decreased liquid yields together with an increase in gas and solid yields (Stefanidis et al., 2011). Bio oil composition can be modified for higher aromatic HC yields (Liu et al., 2014a). They also displayed better catalytic activity during deoxygenation (Liu et al., 2014a). On the other hand, base metal oxides are suitable for ketonization and aldol condensation of carboxylic acid and carbonyl compounds (Liu et al., 2014a). Transitional metal oxides used as catalysts may decrease the liquid organic fraction yield and increase gas, water, and solid yields (Liu et al., 2014a).

Catalytic gasification helps overcomes tar formation by using various *in situ* or *ex situ* catalysts (Chan & Tanksale, 2014; Valderrama Rios et al., 2018). Commonly used gasification are dolomites, which increase gas yields and remove hydrocarbons (Sutton, 2001). Alkali catalysts reduce tar and methane content (Sutton, 2001). Other catalysts used both *in situ* (Chan & Tanksale, 2014) and *ex situ* (Chan & Tanksale, 2014; Sutton, 2001) are nickel based catalyst. They perform better in an *ex situ* process (Sutton, 2001) and are very efficient in hydrocarbons removal and adjustment of the gas composition (Sutton, 2001).

This review aims to present the types of catalysts used and their significance in microwave assisted biomass thermochemical conversion. This review is divided in two categories, catalytic upgrading in pyrolysis and gasification, discussing the two major reactor types; namely, *in situ* and *ex situ* catalytic upgrading, explaining the advantages and disadvantages of each process.

1.1. Microwave Heating Basics

Microwave heating uses electromagnetic energy in the frequency range 300- 3000 MHz and it is used to heat dielectric materials. Microwaves used in industrial and domestic applications in the US operate at 2.45 GHz and 915 MHz (Fernandez, 2015; Mushtaq et al., 2014). Microwaves cause molecular motion by migration of ionic species and /or rotation of dipolar species (Haque, 1999) resulting in dielectric heating. The electric field component of the microwave radiation interacts with the charged particles of the irradiated material (Fernandez, 2015). Microwave heating involves either dipolar polarization mechanisms or space charge polarization mechanisms. Compared to conventional thermal heating, microwave heating has several advantages. Conventional heating has an external heat source where heat is transferred from the surface towards the center of the material by conduction, convection, and radiation; this type of heating system is relatively slow and inefficient. On the other hand, the dielectric heating is a direct conversion of microwave energy into thermal energy. Microwaves can penetrate materials and dissipate energy; therefore, heat is generated throughout the volume of the materials rather than an external source (in-core volumetric heating), making the process more effective due to rapid heating, quick start-up and stoppage or reduced processing time (Fernandez, 2015). A thorough comparison of microwave vs conventional reactors for thermochemical processes is available in the literature. (Domínguez et al., 2007) compared microwave and conventional reactors for pyrolysis of coffee hull and noted that microwave pyrolysis produced more gas and less oil, however, the gas obtained had higher H_2 concentration and low CO_2 concentration. The resulting char had higher porosity and lower oxygen content for microwave process. In general, oil fractions obtained from microwave pyrolysis have higher carbon content and heating values and lower oxygen content than conventional products (Huang et al., 2016).

1.2. Microwave Catalytic Reactors

1.2.1 Microwave catalytic pyrolysis reactors: A typical microwave pyrolysis reactor consists of microwave cavity, gas condensing system, char collector, and vent for incondensable gases (Figure 2). Catalytic biomass pyrolysis is performed either *in situ* (Chen et al., 2018b; Maisano et al., 2017; Vekes Balasundram, 2017), by mixing the catalyst with the feedstock, or *ex situ* (Hu et al., 2017; Wang et al., 2018), by upgrading the pyrolysis vapors using an external catalytic reactor, generally heated at the desired temperature. Microwave reactor designs reported in the literature include both fixed bed reactors (Ma et al., 2017) and fluidized bed reactors (Salema & Ani, 2011). However, fixed bed bench scale microwave reactors are most commonly reported mainly because of its simplicity (Ma et al., 2017). For a fixed bed reactor either one or both biomass or catalyst are placed in the microwave cavity in a fixed bed system during pyrolysis. (Ma et al., 2017) reported a fixed bed in situ quartz beaker-shaped reactor placed within a microwave cavity (Figure 3a). The microwave used was a 2450 MHz frequency, 1 kW generator system. A fluidized bed microwave pyrolysis reactor was reported by (Salema & Ani, 2011), The reactor vessel was a quartz glass tube facilitated with perforated steel distributor plate of 1 mm holes. The quartz tube was equipped with glass caps on both ends with openings for gas flow. The microwave generator was a 1 kW system operated at 2450 MHz frequency (Figure 3b). Microwave gasification reactors are similar to pyrolysis reactor with minor adjustments (Figure 2c). A typical microwave gasification system consists of microwave generator, quartz reactor, temperature measuring unit, gas flow controller, steam vapor producer and product-collecting unit. (Li et al., 2016) reported on an elaborate microwave gasification system. The quartz reactor was equipped with an air distribution plate at the bottom which acted as a catalyst holder. The reactor was completely sealed with PTFE flanges. The reaction gases with known mass fractions were thoroughly mixed in a gas mixer and sent to the reactor with steam. The outlet gases were collected in the collection system outside the reactor.

Multimode microwave cavities were most commonly reported with an exception of few that studied single mode reactors (Li et al., 2016) and travelling wave reactors (Muley et al., 2016). This could be because most domestic and commercially available microwave systems are multimode, 2450 MHz generators with power rating varying from 1-3 kW. One of the challenges with microwave reactor design is temperature measurement during reaction since conventional metal temperature sensors cannot be used in microwave reactor. Fiber optic probes or IR pyroprobes are commonly used (Li et al., 2016; Ma et al., 2017; Muley et al., 2016). Since fiber optic probes have limited temperature range, IR sensors are more often used for high temperature thermochemical processes. To validate the temperature reading from the IR sensor, a portable thermocouple reading is often recorded once the generator is shut off.

2. **Catalyst Used in Microwave Assisted Pyrolysis**

Catalytic upgrading in microwave assisted pyrolysis can be divided into two major groups, namely catalyst mixed together with the biomass (or other samples subjected to pyrolysis) in the same reactor, commonly known as *in situ* upgrading (Figure 2a) (Ma et al., 2017) and catalysts heated in a separate reactor from pyrolysis reactor known as *ex situ* upgrading (Figure 2b) (Liu et al., 2017). During *ex situ* upgrading, catalyst is either placed in parallel within the same microwave oven used for biomass pyrolysis (Zhang et al., 2015a) or an altogether separate microwave reactor (Fan et al., 2017c; Liu et al., 2017; Muley et al., 2016). The volatiles formed during pyrolysis pass through the catalytic reactor while still in gaseous form and are upgraded before they condense (in pyrolysis) or storage (in gasification reactions). The drawback of this method is that the line connecting the catalytic and the pyrolytic reactors need to be heated to prevent inline condensation. In case where the catalyst bed is inside the oven, but separated from the biomass, microwave absorbers should fill the space between the two in order to maintain, a certain temperature that will prevent condensation of gases. On the other hand, the recovery of the catalyst is facile and thus their reactivation can be done if necessary.

2.1. In Situ Catalytic Upgrading

In situ catalytic upgrading is more commonly used than *ex situ* upgrading. In *in situ* upgrading, the catalysts react directly with the pyrolyzed vapors as they are being generated, resulting directly in the upgraded product. The major disadvantages of *in situ* catalytic upgrading is difficult catalyst recovery and, larger catalyst quantity (Wang et al., 2016). A large class of catalysts used in *in situ* upgrading consists of zeolites, metal oxides, and carbon-based catalysts. either used in their existing form or modified with metals.

Zeolites

Zeolites have been shown to be effective in bio oil up-grading via deoxygenation of pyrolysis vapors and promoting formation of aromatic hydrocarbons. The mechanism of bio oil upgrading when using zeolites include series of reactions such as decarboxylation, dehydration, decarbonylating and aromatization (Mullen & Boateng, 2010), resulting in formation of hydrocarbon rich fuel. (Fan et al., 2017b) described the advantages of using zeolites in pyrolysis processes. They state that a temperature of 550-650 °C is optimal for obtaining the highest yield of bio oil from lignin. They noted that the acidic strength and pore size of the zeolite plays an important role in bio oil upgrading. The acidity of the zeolite increases as the Si/Al ratio decreases and the aromatization ability of zeolites also increases. There are many types of zeolites used as catalysts, including HZSM-5, H-Ferrierite, H-mordenite, HY, however HZSM-5 has been found to have stronger acidity and thus is most widely applied for the production of deoxygenated compounds.

(Wang et al., 2016) investigated the modification of HZSM-5 with ethylene diamine tetra acetic acid, catalyst regeneration and its effects on product distribution of upgraded bio oil from microwave pyrolysis. They used a microwave power of 750W, a fixed bed reactor with the catalyst on top of the feedstock (mushroom waste) and SiC as microwave absorbent. The catalyst/biomass ratio was of 1/1 and the pyrolysis temperature was 550°C. They observed a decrease in the liquid products and an increase in gases and water for catalytic process. Product analysis revealed that the liquid fraction is mainly composed of acids, followed by hydrocarbons. HZSM-5 and modified HZSM-5 possessed high selectivity towards alcohols and sugars and low selectivity towards esters, ketones and phenols. Hydrocarbon yield increased with the use of both HZSM-5 and modified HZSM-5. In the latter case the authors found that a catalyst modification for two hours showed the best results.

(Fan et al., 2017a) studied fast microwave-assisted catalytic co-pyrolysis of lignin and LDPE (Low density polyethylene) with HZSM-5 and MgO as the catalyst. They used HZSM-5 for its selectivity to aromatic compounds and its deoxygenation ability. MgO was used also for its deoxygenation capabilities and its selectivity for the alkylation of phenols. They used a microwave power of 750 W, 500 g of silicon carbide as microwave absorbent and the system was kept under vacuum. The pyrolysis temperature was between 450 and 600 °C. In each experiment they used 15 g of feedstock (lignin and LDPE) with or without the addition of catalyst. In order to test various possibilities, the authors have used multiple feedstock catalyst and feedstock to catalyst ratios, as it follows: lignin to LDPE ratio (only lignin, 3:1, 2:1, 1:1, 1:2 and only LDPE), MgO to HZSM-5 ratio (only MgO, 1:2, 1:1, 2:1 and only HZSM-5), and feedstock to catalyst ratio (only feedstock, 1:2, 1:1 and 2:1). For a general ratio of 1:1 (feedstock/catalyst, MgO/HZSM-5, lignin/LDPE) the authors found that the optimum pyrolysis temperature in order to obtain the highest bio-oil yield (32%) was 500 °C. The authors noticed that with increasing temperature the char yield decreases. Phenols decreased with increasing temperature at first but then increased (doubled) at 600 °C, while aromatics showed an opposite behavior. In terms of catalyst ratios, the authors observed that with increasing metallic oxide to zeolite ratio, the proportion of aromatics in the liquid fraction decreased. When the catalyst ratio was unity, no aldehydes, ketones and furans or chain hydrocarbons were found, but they could be observed when HZSM-5 was twice the quantity of MgO. When the authors used just the zeolite as catalyst only chain hydrocarbons were formed. The phenolic compounds increased when both catalysts were used and the catalyst ratio was unity compared with the case when either MgO or HZSM-5 were used by themselves. When no catalyst was used, chain hydrocarbons represented the main fraction while with the addition of catalysts the aromatics increased from 28% to 77% (feedstock/catalyst = 2/1). When the feedstock/catalyst ratio was lower than 1/1 no hydrocarbons or aldehydes, ketones and furans were found. Thus, the authors concluded that MgO promoted the alkylation of phenols and HZSM-5 the formation of aromatics.

2.1.1. Metal Oxides

Other commonly used compounds used as *in situ* catalysts are various metal oxides. Yu et al., (Yu et al., 2014) tried to elucidate in their research the role of metal oxide catalysts on microwave induced pyrolysis using as feedstock sewage sludge. Their study included CaO, $CaCO_3$, NiO, Ni_2O_3, γ-Al_2O_3 and TiO_2 and the experimental set-up was made up of a microwave oven of 700 W maximum power, obtaining temperatures up to 660 °C. They used 30 g of sewage sludge mixed with10 % microwave absorber, and a biomass to catalyst ratio of 10/1. They noticed that when CaO was used as catalyst the highest proportion of hydrogen and the lowest proportion of carbon dioxide was obtained. Also, methane decreased comparing with the case without catalyst. Calcium carbonate was partly decomposed to calcium oxide and carbon dioxide. The proportion of methane was very low at low temperatures, while at high temperatures carbon monoxide and carbon dioxide increased while hydrogen decreased. When nickel-based catalysts (NiO, Ni_2O_3) were used, the researchers obtained increased yields of CO and H_2 and lower yields of CH_4 and CO_2 compared to the case of no catalyst addition. Also, with nickel-based catalyst the proportion of H_2, CO and CH_4 (combustible gases) together was of approximately 65% of the gases obtained in the pyrolysis experiment. As far as alumina and titanium dioxide were concerned, the authors noticed from the pyrolysis experiments that low temperatures had no significant effect versus no catalyst at all. At high temperatures, when γ-Al_2O_3 was used they observed an increase in the methane and hydrogen content versus no catalyst, while TiO_2 had no significant effect in terms of gas composition, though total gas yields increased.

Huang et al., (Huang et al., 2013) aimed to study the performance of microwave pyrolysis of corn stover using metal oxide catalysts in a 500W microwave reactor purged with N_2/CO_2. The catalysts used were NiO, CaO, MgO and CuO. The pyrolysis temperature was between 450-520 °C depending on catalyst and atmosphere. All catalysts had similar reaction products. The authors noticed that 3% catalyst is optimum to obtain the highest temperature inside the reactor. The production of gases (CO_2, CO, H_2, CH_4) was lower when using catalyst in comparison to the experiments without catalyst. Also, the liquid fractions had fewer ring aromatics, with phenol and methylnaphthalene being the main constituents. The authors concluded that the addition of catalysts should restrain the formation of polycyclic aromatic hydrocarbons (PAHs) in the pyrolysis products.

In one of their latest work Kuan et al., (Kuan et al., 2013) studied the catalytic effect on microwave pyrolysis of sugarcane bagasse using metal oxides (NiO, CuO, CaO, MgO), also in a 500 W microwave reactor. Approximately 3 to 5 g of feedstock was used along with the catalysts in three proportions, 3, 5 and 10%, respectively. The reaction temperature was between 490 and 532°C depending on the catalyst and its ability to function as a microwave receptor. When using catalysts, the production of gases was slightly modified, with NiO and CaO being conducive for the formation of syngas. On the other hand, CuO or MgO decreased the production of syngas. A general rule was that all catalyst decreased the production of methane. Doing a quantitative analysis, the authors came to the conclusion that NiO and CuO increased the liquid fraction and CaO or MgO increased the gaseous fraction. Without catalyst they obtained a relative weight percentage of solid, gaseous and liquid products of 19, 58 and 23 wt%, respectively, while by adding catalysts they found that the proportion gaseous products under the addition of NiO, CuO, CaO, and MgO were about 52, 53, 62, and 65 wt% and the average percentages of liquid products under the addition of NiO, CuO, CaO, and MgO were about 32, 33, 24, and 18 wt%. Other reported studies with metal oxides as catalysts include that of Ma et al.,(Ma et al., 2017), which used CaO and Fe_2O_3 in the microwave pyrolysis of sludge for bio-fuel production. The pyrolysis temperature was between 500-900 °C, using 30 grams of sludge and 10 wt% catalyst. Comparing with the case without catalysts at 900 °C char yield decreased from 60.4% to 55.3% and 51%, respectively when Fe_2O_3 and CaO were used. On the other hand, the gas yield increased with increasing temperature. The highest proportion of gas was obtained at 800 °C (35.1%) with CaO, far higher than in the case with no catalyst addition (23% at 900°C). The highest amount of gas when using Fe_2O_3 catalyst was obtained at 900°C (29.5%) comparing with only 23% without catalyst. The highest bio-oil yield was obtained with Fe_2O_3 (20.4% at 700 °C) versus no catalyst (18.4%). Liquid yields with CaO were lower than without catalyst between 600 and 800°C and slightly higher at 500 and 900°C. The qualitative analysis revealed that the maximum content of the aliphatic hydrocarbons was obtained at 900 °C when using CaO as catalyst, which was 15.7% comparing with 12.3% when Fe_2O_3 was used and only 9.2 % without catalyst. Highest yield of aromatics was obtained at 800 °C, with a maximum of 16.7% when CaO was used, almost twice than when no catalyst was added. Also, at this temperature and with CaO addition, 12% aliphatic hydrocarbons were obtained. They concluded that 800 °C is the best temperature to be used when adding CaO catalyst in terms of bio oil up-grading, while 900 °C was considered to be the best temperature for maximum bio oil yield. The study emphasized that with increasing temperature the hydrogen and methane production increases when using either catalyst compared to the absence of catalyst. The authors surmised that CaO was better suitable for the production of syngas while Fe_2O_3 was better for the production of bio oil.

In their article, Mushtaq et al., (Mushtaq et al., 2014) reported the use of metal oxide catalysts on microwave assisted pyrolysis of coal and biomass for fuel production. The authors state the importance of using microwave absorbents in microwave assisted pyrolysis processes due to the fact that the majority of the used feedstock have low microwave absorption. The authors emphasize that metallic oxides can be a reliable class of microwave absorbent materials due to the fact that they can increase the heating rate and can also interact immediately with both condensable or non-condensable gases, having a dual effect, as microwave absorbents and catalysts. Among the various metal oxide catalysts used in coal pyrolysis, the authors noticed that Fe_3O_4 was found to enhance the syngas yield and regarding the catalyst ability to crack aromatic and aliphatic hydrocarbons the authors reported that the order of efficiency is Fe_3O_4, $>Al_2O_3$, $>CaO>SiO_2$, >quartz bead.

Morgan et al., (Morgan et al., 2017) described the importance of using metal oxides, zeolites and/or other microwave absorbents in pyrolytic processes. The study noticed that the most used metal oxide catalysts are NiO, CaO, CuO and MgO, generally used *in situ* and seldom *ex situ*. Their study also state that these catalysts usually increase the ratio of mass loss and thus they have a positive effect on gas and liquid yields. Generally, it was noted that CuO or MgO can increase the H_2 content, while CaO and MgO may have a positive effect on overall gas production. Also, NiO or CuO can be used to augment the liquid production. As far as the reaction environment is concerned, the study concluded that the alkali earth metal oxides catalysts under N_2 atmosphere performed better than under CO_2 atmosphere, maybe due to the difference in the radiation absorption of CO_2 and N_2. The authors noticed that metal oxides or zeolites are widely used as catalysts and microwave absorbents, while SiC and activated carbon are mostly used as absorbents in microwave assisted pyrolysis.

In their report on microwave pyrolysis of lignocellulosic biomass Huang et al., (Huang et al., 2016) concluded that almost 50% of the biomass can be converted to gas products (H_2, CH_4, CO, and CO_2) at moderate to high temperatures. The high H_2 and CO yields from microwave pyrolysis result in gases with greater heating value than gases from conventional pyrolysis. It was also observed that the addition of proper catalysts can greatly influence product selectivity and yields of microwave assisted pyrolysis. Addition of NaOH, Na_2CO_3, Na_2SiO_3, NaCl, TiO_2, HZSM-5, H_3PO_4, and $Fe_2(SO_4)_3$ results in higher solid yields on one hand and lower gas yields, on the other hand, having no substantial effect on liquid yields(Chen et al., 2008). The addition of KAc, Al_2O_3, $MgCl_2$, H_3BO_3, and Na_2HPO_4 has a double purpose, both as a catalyst and as microwave absorbents to speed up the heating rate of the reaction and overall temperature.

Wan et al., (Wan et al., 2009) evaluated product selectivity of microwave-assisted pyrolysis of cellulosic materials by using metal oxides and chloride salts as catalysts They investigated multiple catalysts: $K_2Cr_2O_7$, Al_2O_3, KAc, H_3BO_3, Na_2HPO_4, $MgCl_2$, $AlCl_3$, $CoCl_2$, and $ZnCl_2$. The biomass/catalyst mixture was subjected to microwave pyrolysis for 20 minutes, using a microwave power of 875 W and reaching temperatures between 450 and 550 °C. That study found that liquid yield is increased by addition of KAc, Al_2O_3, $MgCl_2$, H_3BO_3, and Na_2HPO_4 catalyst. Moreover, KAc also reduces the solid yield without any changes in gas production. In contrast with the addition of Al_2O_3, the increase in the liquid yield comes with a decrease in gas yield. On the other hand, for $MgCl_2$, H_3BO_3, and Na_2HPO_4 it was observed that the increase in the liquid yield results in decrease in both solid and gas yields. Na_2HPO_4 results in high bio oil yield with a large reduction of solid yield and less reduction of gas yields while $MgCl_2$ and H_3BO_3 increases bio oil yield at the expense of gas production. The authors observed that all chloride salts used in their experiments promoted the production of furfural.

Moen et al., studied (Johannes Moen, 2009) the effect of certain catalyst and catalyst groups on the fraction yields and properties in microwave assisted pyrolysis of biomass. That used 800 W of microwave power (from a 1000 W oven) in order to obtain temperatures between 560 and 620 °C and pyrolyzed 250 grams of biomass mixed with 2% catalyst. They used aspen pellets biomass and various catalyst types, such as chlorides (NaCl, KCl, $CaCl_2$, $MgCl_2$, $AlCl_3$, $ZnCl_2$, $FeCl_2$, $FeCl_3$, $SnCl_2$, $CoCl_2$ and NH_4Cl), nitrates ($Mg(NO_3)_2$, $Fe(NO_3)_3$, $Cu(NO_3)_2$, $AgNO_3$, $Ni(NO_3)_2$, $La(NO_3)_3$, $Te(NO_3)_4$, $Rh(NO_3)_3$ and $Co(NO_3)_2$) and metal oxides (MnO_2, ZrO_2, Al_2O_3 and MgO). After the experiments the authors compared all the yields and noticed that chlorides resulted in highest liquid fractions (41% compared to 35% without catalyst) but most of the increase was in the water phase residue. On the other hand, with metal oxides resulted in the highest bio oil yield (23% versus 19% without catalyst). The authors tested the miscibility of the obtained light oils with diesel fuel using n-butanol as solvent and obtained promising results. Liu et al.(Liu et al., 2014b) described a series of experiments concerning microwave pyrolysis of food waste. The study monitored different characteristics and reaction products obtained after using metal oxides and chloride salts as catalysts. Microwave power up to 4000 W was used (400 W was determined to be optimum), 30 grams biomass with 5% catalyst. As catalysts MgO, Fe_2O_3, MnO_2, $CuCl_2$ and NaCl were used. They noticed that MnO_2 and MgO had beneficial effects in the pyrolysis experiments by increasing the maximum temperature and heating rates. On the other hand, other oxides decreased the heating rates due to their poor microwave absorbency. Authors noticed that the solid yield increased to almost 80% when CaO and CuO were used, obtaining 13% bio oil, with balance as the gas fraction. Addition of the other oxides resulted in a decrease in the bio oil yield and an increase in the gas yields. $CuCl_2$ proved to be a suitable catalyst, increasing the heating rate and obtaining higher gas yields. The study concluded that MgO, MnO_2 and $CuCl_2$ work as catalysts in microwave pyrolysis of food waste, NaCl has almost no effect while CuO, CaO and $MgCl_2$ worsen the pyrolytic process in terms of temperature achieved, heating rates and reaction products.

2.1.2. Carbon-based catalysts

Besides zeolites or metal oxides other materials or combinations of materials are also used as *in situ* catalyst in microwave assisted pyrolysis processes of various feedstocks. Carbon-based materials are good candidates for catalysts used in microwave assisted pyrolysis due to the fact that they can act both as catalysts and microwave absorbers. Bu et al., (Bu et al., 2014) used lignin for production of renewable phenols and fuel by catalytic microwave pyrolysis. This study used a microwave power of 700 W, 20 grams of lignin as feedstock and between 31 and 88 grams of activated carbon as microwave absorbent and catalyst. The reaction temperature ranged between 350 and 600 °C. It was observed that the bio oil yield ranged between 18.5 % at 350 °C up to 41.5 wt% at 450 °C. The gas yield showed an increasing trend with increasing temperatures and ranged between 10.27–45.5 wt% (at 591 °C). Solid yields decreased with increasing temperatures. To see the catalyst effect, the authors performed non catalytic tests and concluded that activated carbon increases the bio oil yield from 15% to a maximum of 41.5% but decreases the gas yield from a maximum of 55% without catalyst to a minimum of 10% with activated carbon. The addition of catalysts also increased the char yield from 30% without catalyst to 55 % with catalyst when the reaction took place at lower temperatures. The authors reported that the bio-oils consisted in phenols, guaiacols, hydrocarbons and esters (71–87% of bio-oils), with 550 °C being the optimum temperature to obtain the maximum amount of phenol and phenolic compounds.

Zhang et al. (Zhang et al., 2015b) studied microwave pyrolysis of rice husk to maximize gas yield with high quality syngas. They used rice husk char supported by metals as catalysts in a 700 W microwave reactor. Fifty grams of rice husk was mixed with 15 grams of catalyst (rice husk char (RHC) or rice husk char supported with Cu, Fe and Ni). The authors observed that the gas yield increased to 54 % with catalytic upgrading, while the liquid yield decreased. Ni/RHC was considered to be the best catalyst in terms of gas production due to the fact that $CO+H_2$ proportion was about 70%, with a H_2/CO ratio of 1.09. The liquid fraction was composed mainly of acids, ketones, furans, phenols and sugars. The addition of catalysts resulted in the increase in acids and ketones while aromatic organic compounds and sugars decreased.

Char based catalysts were used by Omoriyekomwan et al.,(Omoriyekomwan et al., 2016) in phenol production from biomass pyrolysis using a 2000 W microwave generator. Seven grams of palm kernel shell biomass were pyrolyzed in a microwave heater with activated carbon or lignite char as catalysts in proportions of 10% and 20% respectively. The authors tested the pyrolysis effect at three temperatures, 400, 500 and 600 °C. When experiments were performed without catalysts no more than 200 °C were achieved in the microwave reactor since biomass is a poor microwave absorber. Temperature of 600 °C was achieved with the addition of catalysts and an increase in the heating rate of 200 C/min was achieved with lignite char as catalyst. Highest heating rates were observed when the biomass/catalyst ratio was 20%. At this ratio, at 500 °C, highest bio oil yield, almost 37%, was also obtained. With activated carbon as catalyst, 23 to 29 % liquid fraction yield was achieved. Char yield was between 24 and 52 wt% in all conditions. The bio oil was rich in phenolic compounds. Besides, low concentrations of cyclopropylcarbinol, creosol, 1H-indene,1-methylene-catechol and 1,2,4-trimethoxy benzene were also obtained. When using activated carbon, the authors got a better selectivity of phenolic compounds, obtaining 4.13 mg/g compared to a maximum of 2.89 mg/g when lignite char was used.

Hu et al.,(Hu et al., 2012) studied the effect of microwave power levels and the influence of catalysts in the microwave assisted pyrolysis of microalgae, *Chlorella vulgaris*. 5 and 30 % catalyst (activated carbon, CaO, SiC and solid residue) were added to 30 grams of feedstock at various microwave powers: 750 W for 220 °C, 1500 W for 600 °C and 2250 W for 750 °C. Maximum bio oil yield (35.8%) was obtained at 1500 W and the maximum gas yield (53.4%) was achieved at 2250 W.

Dong et al. (Dong et al., 2018b), studied in one of their latest articles, microwave pyrolysis of moso bamboo using as catalyst activated carbon (AC) -supported iron(III). Their tests were of *in situ* type; they used a power of 600 W (from a 3600W microwave reactor) for 20 minutes, obtaining temperatures between 400 and 600°C. The mixture to be pyrolyzed contained moso bamboo and 5%, 10%, 20% and 50% catalyst. Tests with bamboo mixed with activated carbon were performed for comparison reasons. A higher gas yield was noted (up to 65% more) when catalyst was used, compared with the case with plain activated carbon, with a proportional drop in the bio oil yield. The authors concluded that the catalyst improved the content of syngas, reaching 81 vol%, with a H_2/CO ratio of 1.04 and inhibited CH_4 and CO_2 production.

In a separate work on moso bamboo biomass, Dong et al. (Dong et al., 2018a) compared *in situ* conventional pyrolysis using bamboo char catalyst to microwave assisted pyrolysis of the same biomass (catalyst ranging from 5 to 20%). In the conventional process they used a pyrolysis temperature of 700 °C for 20 minutes while in the microwave system 600 W of power for 20 minutes were used to achieve 670 °C with catalyst (about 46% more than the case without catalyst). In microwave assisted pyrolysis, the authors observed that bio-oil yield decreased by increasing the rate of catalyst addition (vs. no catalyst), favoring the formation of gases, while in the case of conventional pyrolysis the yields were similar to the situation when 20% catalyst was used in microwave assisted pyrolysis. After bio oil analysis the authors noticed that the addition of bio char results in bio oils with acetic acid and phenols as main constituents (ranging from 73% up to almost 83%). Also, an increase in C_2-C_6 compounds was observed, thus the authors suggested that biochar was favorable to the conversion of the heavy compounds into the relatively lighter species. The phenol content also increased from 1 to almost 24% under microwave irradiation after adding bio char. In the end, it was concluded that bio char is more effective in up-grading bio oil and in syngas production when using microwave radiation that conventional heating. They reported a syngas production reaching 65% with 20% biochar addition in microwave heating compared with 60% in conventional pyrolysis.

Chen et al. (Chen et al., 2018a) investigated in their work *in situ* microwave-assisted co-pyrolysis of *Chlorella vulgaris*, wood sawdust and their blends using AC or SiC as the additives. They used a microwave power of 1000 W for 25 minutes, obtaining temperature up to 800 °C, and used 10% catalyst (AC or SiC). After experiments the authors noticed the following aspects: liquid yield was higher when SiC was used; using additives had a positive effect on aromatization and deoxygenation; when wood sawdust was pyrolyzed and SiC was used as additive they obtained good selectivity towards phenols; when using AC as additive the authors noticed that aromatic hydrocarbons decreased and aliphatic hydrocarbons increased if increasing the *Chlorella vulgaris* proportion; when using a mix of 30 % sawdust and 70 % *Chlorella vulgaris* a high selectivity of alkanes was reached.

2.1.3. Other catalysts

Chen et al. (Chen et al., 2008) studied catalytic microwave pyrolysis of pinewood sawdust using various inorganic additives and they monitored their effect on solid, liquid and gas yields distribution. An initial microwave power of 1000 W was used until the desired temperature was reached, the temperature was subsequently maintained via pulse microwave at 300 W during the remaining of the experiments. The feedstock (saw dust) was wet impregnated with 10 % catalyst. They used SiC as microwave absorbent resulting in a biomass (or biomass/catalyst) and SiC layers in a sandwich formation. The system was purged with argon and the desired pyrolysis temperature was of 470 °C. The authors observed that all catalysts (NaOH, Na_2CO_3, Na_2SiO_3, NaCl, TiO_2, HZSM-5, H_3PO_4, $Fe_2(SO_4)_3$) increased the char yields. $Fe_2(SO_4)_3$ and NaCl favored the liquid yield. The other catalysts did not have significant effect on the liquid fraction. The authors also observed that all catalysts decreased the total gas yields. NaOH, Na_2CO_3, Na_2SiO_3, HZSM-5 and H_3PO_4 increased the hydrogen yields while NaOH, Na_2CO_3, NaCl, TiO_2, H_3PO_4

and $Fe_2(SO_4)_3$ decreased the CO yield. All the sodium containing catalysts favored acetol formation, while the strong bases (NaOH, Na_2CO_3 and Na_2SiO_3) had a negative effect in the formation of 4-methyl-2-methoxyphenol, furfural, 2-furanmethanol and levoglucosan. The study also noticed that HZSM-5 has no effect on the formation of acetol while TiO_2 restrains its formation. When H_3PO_4 and $Fe_2(SO_4)_3$ were used as catalysts the dominant components in the liquid fractions were furfural and 4- methyl-2-methoxy-phenol.

In their work (Lin et al., 2012) Lin et al. operated a pilot scale microwave pyrolizer that produces bio oil from sewage sludge. The study investigated how various factors such as heating rate, temperature and catalysts affect the quality of the obtained bio oil. The set-up included 12 magnetrons of 800 W each, the feedstock was prepared by impregnating the biomass with 5 to 7 % catalyst, the weight of each sample was 3.5 kilograms and the total heating time was 120 minutes. Three pyrolysis temperatures were investigated, 350, 400 and 450 °C, with different catalysts; KOH, H_2SO_4, H_3BO_3, $ZnCl_2$, and $FeSO_4$. It was observed that KOH improves the quality of the liquid fraction, resulting in the highest calorific value and carbon content while possessing the lowest nitrogen quantity. On the other hand, H_3BO_3 and H_2SO_4 also augmented the calorific value and carbon content but resulted in high nitrogen fractions as well. The calorific value of the bio oil was enhanced by FeSO4, while $ZnCl_2$ had a negative effect. The authors mention that with $ZnCl_2$ high quantities of sulfur were found in the bio oil. As the composition of the obtained bio oil is concerned, the authors found that KOH increased the quantity of alkanes and monoaromatics while H_2SO_4 and H_3BO_3 favored the obtaining of ketones, alcohols, heterocyclics and nitriles. The study also concluded that all the used catalysts decreased the density and viscosity of bio oils.

In situ catalytic tests resulted in more quality reaction products comparing with non-catalytic experiments. When zeolites were used, less liquid fraction was obtained, but of higher quality. HZSM-5 with low Si/Al ratios improved the production of aromatics (Fan et al., 2017a; Fan et al., 2017b). When metal oxides were used the results varied. Nickel oxides may increase the syngas production (Kuan et al., 2013; Yu et al., 2014). Iron oxides can decrease the liquid yield (Liu et al., 2014b) but can be efficient in CH_4 production in some cases (Ma et al., 2017). CaO may decrease the liquid yield but improve its quality and also be efficient in H_2 production (Ma et al., 2017). Carbon based catalysts resulted in higher heating rates (Omoriyekomwan et al., 2016). When improved with metal additions, the quantity of syngas increased (Dong et al., 2018b; Zhang et al., 2015b). Activated carbon catalyst resulted in bio-oil yields up to 41% (Bu et al., 2014) . Each catalyst type has its own advantages, zeolites are generally inexpensive and are efficient in deoxygenation reactions but could have poor microwave absorbance, while metal oxides or carbon-based catalysts can act as microwave absorbents and some are efficient in syngas production (Dong et al., 2018b; Mushtaq et al., 2014; Zhang et al., 2015b).

2.2. Ex-Situ Catalytic Upgrading

Ex situ catalytic upgrading is less commonly used than the *in situ* as they require additional procedures to the pyrolytic set-up, such as heated gas lines, additional temperature controllers or catalytic reactors. However, *ex situ* processes have multiple advantages over *in situ* upgrading. One major advantage of *ex situ* method is the ability to adjust the catalyst temperature independent of pyrolysis temperature (Liu et al., 2017). When the catalyst is separately heated from the biomass, its recovery is much efficient, and an optimal catalyst bed temperature can be obtained.

2.2.1. Zeolites

Liu et al., (Liu et al., 2017) presented a sequential two-step catalytic fast microwave assisted pyrolysis of biomass through a packed-bed HZSM-5 (Si/Al=80) catalyst for high quality bio-oil production. The microwave reactor was operated at 750 W and 500 grams of SiC was used as a microwave absorbent to heat the biomass (corn stover). The authors observed that in order to obtain the maximum bio oil yield (33.8 wt.%) with the maximum proportion of aromatic compounds (26.2 %), the catalyst bed has to be at 425 °C, the pyrolysis temperature has to be 550 °C with a catalyst to biomass ratio of 1:5. Above 550 °C the bio oil fraction decreases while the gas yield increases. The solid residue has the highest proportion at lower temperatures (29.7 wt.% at 450 °C) and the lowest at higher temperatures (19.6 wt.% at 650 °C). The authors also mentioned that at the optimum temperature of 550 °C, the bio oil contained valuable chemical compounds, such as xylene (3.73%), indene (5.14%), toluene (0.70%), naphthalene (15.62%) and phenol (4.65%). Last but not least they observed that HZSM-5 has good stability in the catalytic upgrading process. The diffractogram comparison (Figure 4 a), (Liu et al., 2017)) of the used and fresh catalyst were similar, the crystal structure and crystallinity of the catalyst remaining intact before and after experiments.

Liang et al., (Liang et al., 2017) compared the quality of the bio oils from microwave (750 W) pyrolysis of rice straw in the presence of zeolite catalysts with various Si/Al ratios or with addition of metals (Co, Zn, Ni). Their study used 30 grams of rice straw as feedstock, 1.5 grams of activated carbon as microwave absorber and 1.5 grams of catalyst used *ex situ*. Cobalt modified ZSM-5, having a Si/Al ratio of 46 had the highest liquid fraction, almost 27%, compared to just 14% without catalyst. Generally, when modified zeolite catalyst was used, higher bio oil yields were obtained. Zinc modified ZSM-5 had similar effect as Co/ZSM-5 while nickel modified zeolite resulted in lower liquid yields compared to the other catalysts, but still higher if compared to non-catalytic experiments. The authors concluded that Zn/ZSM-5 (Si/Al=46) was best in terms of compound selectivity and bio oil production. The GC/MS analysis performed by the authors revealed that the concentration of ketones, aldehydes and phenols was higher comparing with their control experiments (Figure 5).

Zhang et al. (Zhang et al., 2015a) investigated the catalytic bio oil upgrading from microwave pyrolysis of corn stover using a modified HZSM-5 catalyst. 750 W microwave power were used to reach a pyrolysis temperature of 500 °C for a total reaction time of 45 minutes. SiC was used as microwave absorbent, 5 grams of corn stover as feedstock and 0.25 grams of catalyst (also mixed with some silicon carbide particles). In this case the catalyst was placed in the same microwave cavity, so there was no need for its additional heating, and the catalysis (using HZSM-5 and silanized HZSM-5 – SiO_2-HZSM-5) occurred at a temperature estimated to be the same as pyrolysis. Solid yield decreased when the SiO_2 proportion increased. The obtained bio oil yields were between 15.6 and 22.6 %. When increasing the ratio of SiO_2 up to 3.7%, the study noticed than oxygen containing aliphatic compounds decreased while total hydrocarbons, aliphatic hydrocarbons and aromatic ones increased, but as the SiO_2 ratio increased further, a decrease in the catalytic activity was also seen. Also, an increase followed by a decrease was also noticed in the relative contents of xylene, toluene, benzene and naphthalene. When performing the gas analysis, the authors reported that hydrogen, carbon monoxide, carbon dioxide and methane were present. The highest concentration of syngas was about 33% and the report stated that it could be used as high quality gaseous fuel.

Muley et al., (Muley et al., 2016) performed catalytic upgrading experiments of pyrolysis gas from pine sawdust using microwave heating of a zeolite catalyst and compared the results with conventional heating methods. The pyrolysis experiments were performed in an induction pyrolysis set-up, and the gas was upgraded *ex situ* using HZSM-5 catalyst heated at three different temperatures using microwaves. A catalyst: biomass ratio of 1:2 was used, and it was noticed that liquid yield slightly decreased when the catalyst temperature increased. This amount was lower than in non-catalytic experiments but was comparable to values obtained in conventional heating methods being in the range of 25-35%. The use of catalysts results in a higher yield of aromatic and aliphatic hydrocarbons while the non-upgraded oil was reach in ketones, phenols and alcohol or aldehydes. On the other hand, the gas yield increased as the catalyst bed temperature increased. The gas proved to contain CO (20-23 wt%), CO_2 (10%), CH_4 (up to 6%) and C_2-C_5 gases (below 3%). Hydrogen content was not mentioned in the reported study. A high C/H mole ratio was observed for the coke deposited on the catalyst, indicating that the product is aromatic in nature, and in microwave upgrading this ratio increased with temperature (Figure 4b).

Fan et al.(Fan et al., 2018) compared in their work *in situ* and *ex situ* upgrading of pyrolytic vapors using lignin as feedstock and HZSM-5 as catalyst in a microwave assisted process. The pyrolysis temperature was set at 550 °C. In the *ex situ* process, various catalyst-to-lignin ratios were tested (0.1, 0.2, 0.3, and 0.4) and different catalytic temperatures (250, 350, 450 and 550 °C). In this case the catalyst was outside the microwave oven, in a separate catalytic reactor, heated independently. In the *in situ* process, the biomass and catalyst were uniformly mixed with SiC particles and introduced into the quartz reactor, inside the microwave oven. The authors noticed that 0.3 was the optimal catalyst-to-lignin ratio and 450 °C was the optimal temperature regarding lignin conversion to aromatics. As gas yield is concerned, a drop in CO_2 concentration was observed, coupled with a rise in CO concentration as the catalyst-to-lignin ratio increased from 0 to 0.3. Hydrogen followed a similar trend. A higher catalytic temperature lowered the concentration of CO_2 and increased the concentrations of CH_4 and CO. The authors concluded that *ex situ* upgrading results in lower bio oil yield with higher selectivity towards aromatics, if compared to *in situ* method. The gas yield was similar in both cases, with more syngas and less CO_2 being obtained from the *ex situ* process.

Zhou et al. (Zhou et al., 2018), presented in their study the microwave assisted pyrolysis of corn stover using an *ex situ* catalyst, consisting in ZSM-5 coatings on SiC foam. For comparison reasons various configurations of catalyst placement were tried (one *in situ* and two *ex situ*), as well as a control without catalyst. For *ex situ* configurations the catalyst was placed outside the microwave reactor and it was heated independently. Pyrolysis temperature was 550 °C and the catalyst temperature was 425 °C (for the *ex situ* experiments). *Ex situ* experiments yielded higher quality bio oils in comparison with the *in situ* tests. Thus, the study indicated that considerable amounts of aromatics and significantly lower contents of oxygen-containing aliphatics were obtained. The best results were noted for a composite catalyst bed configuration, with 41.5 % aromatics and just 1.6 % oxygen containing aliphatics. In that configuration the authors obtained almost 19% BTEX (benzene, toluene, xylene). The research team also gave an explanation for the better results obtained in the *ex situ* composite bed catalytic tests, namely, the dispersion of the catalyst in the form of thin layers making it more accessible to pyrolytic vapors. When increasing the catalyst to biomass (0 to ½. the ratio), less bio oil yield was obtained, but with improved quality. The catalyst deactivated after several runs, yielding higher liquid yield after a fifth run, but of lower quality. The catalyst could be regenerated by calcination at 500 °C for 8 hours in air.

2.2.2. Metal oxides

Fan et al., (Fan et al., 2017c) studied *ex situ* catalytic upgrading of the vapors obtained from the microwave pyrolysis of low density polyethylene in order to obtain products of enhanced quality using magnesium oxide as catalyst. Their study used a microwave power of 3000 watts, a fixed catalyst bed, 15 grams of biomass as feedstock and 0.5 kilograms of SiC as microwave absorbent. Different catalyst to reactant ratios (from 1/15 to 1/3) and various pyrolysis and catalytic reaction temperatures from 350 to 550 °C were studied by the authors. The catalytic upgrading resulted in lower liquid fractions (24.2 to 38.5 wt%) compared to non-catalytic pyrolysis (46.3 wt.%). Even though the liquid yield was lower, the quality of the oil was better than the one without upgrading. Produced bio oil contained monoaromatics (15.2% to 50.3%) and C_5-C_{12} aliphatic hydrocarbons (30.2% to 68.7%), depending on tested conditions. Total percentage of gasoline fraction in the obtained liquid was computed to range from 79.5% (37.3% mono-aromatics and 42.2% C_5-C_{12} aliphatics) to 96.0% (39.7% mono-aromatics and 56.3% C_5-C_{12} aliphatics) comparing with the experiments without catalysts (10.5% mono-aromatics and 30.2% C_5-C_{12} aliphatics). Gaseous products were also detected, and they consisted mainly in hydrogen, ethylene, methane, propylene, ethane and propane. In all cases the hydrogen, methane and ethylene quantities were lower when catalyst was used, regardless its proportion while propane, ethane and propylene were obtained in higher fractions comparing with the case without catalyst. That study concluded that higher ratios of catalyst to reactant, higher pyrolysis and catalytic reaction temperatures favored the gas yields.

Zhang et al. (Zhang et al., 2010) described the pyrolytic vapor conversion of aspen pellets using zirconium oxide, 3A and 4A molecular sieve based catalysts. They used 700 watts microwave power, between 50 and 250 grams of sample and a total reaction time of 20 minutes. The catalyst bed was used *ex situ* and was heated between 300 and 600 °C. The authors noticed that molecular sieve-based catalysts had no effect on liquid yield and composition. When using zirconium oxide catalyst (CoO/ZrO_2, NiO/ZrO_2, La_2O_3-ZrO_2, NiO-CaO/ZrO_2, Cl^-/ZrO_2, SO^{2-}_4/ZrO_2, NaO/ZrO_2, CaO/ZrO_2, and MgO/ZrO_2) at a reaction temperature of 350 °C the liquid fraction was slightly increased. Increasing the reaction temperature resulted in a decrease of the liquid yields and an increase of the gas yield. The authors identified as liquid compounds ketones, polycyclic aromatic hydrocarbons, carboxylic acids, aldehydes, esters and nitrogenated compounds, among others

Ex situ catalytic process performed better than *in situ* due to the capability of selecting the optimal working temperature. The use of zeolites resulted in higher quality bio oil compared to non-catalytic tests. Higher proportion of aromatics were obtained while decreasing the contents of oxygen-containing aliphatic compounds (Zhang et al., 2015a). When magnesium oxide was used the bio-oil yield decreased, increasing the total percentage of gasoline fraction (Fan et al., 2017c). Carbon based catalyst were not used in *ex situ* microwave assisted experiments. The vast majority of articles dealing with catalytic microwave assisted pyrolysis use zeolite-based catalysts and more research is necessary with the focus on metal oxides or other catalyst types.

3. Catalysts Used in Microwave Assisted Gasification

Being the product of the gasification process, syngas ($CO+H_2$) presents interest due to its usage as intermediate in the obtaining of several products, such as ammonia, methanol or Fischer-Tropsch fuels(Lv et al., 2007). Generally, syngas is obtained from various fossil fuels but the recent trend tends toward generating it from renewable resources (biomass) or from waste. Syngas production from biomass gasification contains, besides carbon monoxide and hydrogen, also methane, carbon dioxide, light hydrocarbons and in some cases unwanted products such as HCl, H_2S or tar (Xie et al., 2014). In order to overcome the problem of contaminants and to obtain high quality syngas, research focused on the development of catalytic gasification and in using various heating sources. Even though microwave heating was successfully used in pyrolysis experiments, its usage in gasification processes is moderate. Below we present some of the sparse literature reports where microwave assisted catalytic gasification was used.

Li et al., (Li et al., 2016) performed methane reforming by CO_2 and H_2O with bio-char prepared by microwave pyrolysis of cotton stalk at 800 °C for 30 min using bio char as catalyst in a 3 kW microwave generator. A mixture of CH_4, CO_2, N_2 and steam was introduced in the reactor where 3 grams of catalyst was preheated at desired temperature. The authors observed that at the right H_2O/CO_2 ratio the combined reforming augments CH_4 conversion as well as the H_2/CO ratio. They also observed that a H_2/CO ratio of 2 was obtained at a H_2O/CO_2 ratio of one half and noticed that if the temperature increases, CH_4 reforming increases as well. The performance of the bio-char used as catalyst in reforming reactions decrease in time due to a reduction in surface porosity of the catalyst.

Pooya Lahijani et al. (Lahijani et al., 2015) studied biomass char gasification derived from oil palm shell using microwave irradiation. The set up used 1150 W microwave power, 10 wt% ash-loaded char as catalyst and oil palm shell and empty fruit bunch as feedstock. An 8 g sample was gasified at 750 and 900 °C in presence of CO_2. They obtained 93% CO yield, as opposed to 58% without the addition of catalyst.

Fernandez et al. (Fernández et al., 2010) focused on dry and steam reforming of glycerol using microwave heating and carbon type catalysts. The experimental temperature was 800 °C. The study used activated carbons catalyst, which also acted as microwave receptor. Twelve grams catalyst and 40 mL/h flow rate of glycerol in nitrogen inert atmosphere were used. The authors compared the influence of heating source on the conversion of glycerol under catalytic gasification. It was noticed that microwave heating, compared to electrical heating, results in higher glycerol conversion in terms of H_2 and syngas production. Activated carbon also appeared to be suitable for producing syngas having a H_2/CO ratio of almost one with very small amounts of CO_2.

Xiao et al., (Xiao et al., 2015) applied microwave heating for steam gasification of rice straw biochar using alkali and alkaline earth metals as catalysts at temperatures between 550 and 800 °C. Three different catalysts were tested; K_2CO_3, KOH, $Ca(OH)_2$ mixed with 3 grams of biochar. Catalyst quantity was between 5 and 10 % and were added to biochar by physical mixing. The flow rates for nitrogen and steam were 40 mL/min and 0.1 mL/min, respectively. The authors compared conventional and microwave gasification processes and investigated the effects of the catalysts. It was observed that KOH and K_2CO_3 augment not only the conversion, but also the CO_2 percentage. On the other hand, $Ca(OH)_2$ had lower conversion efficiency and lower contents of CO_2. With 10 % $Ca(OH)_2$, 94.3 vol.% syngas was obtained, compared to 92.5 % without catalyst. The study concluded that microwave heating performed better than conventional heating, reducing the reaction temperature by 200 °C, with similar results.

Long et al. (Long et al., 2014) studied the possibility of reusing the catalyst from transesterification reaction in hydrothermal gasification of by-product glycerol (formed during a transesterification reaction) together with Ni catalyst. First part of their study was microwave assisted transesterification of Jatropha and rapeseed oils in presence of sodium silicate catalyst. The catalyst from this process was reused in gasification reaction with the addition of Ni. Since the hydrogen yield with sodium silicate alone was low, Ni was added to improve the H_2 yields. 83% hydrogen yield was obtained from gasification of pure glycerol and 85 % yield with crude glycerol (from biodiesel production after distillation) under optimized conditions - sodium silicate (160 wt.%) and Ni catalyst (40 wt.%). To study the recyclability of the catalyst the authors compared XRD patterns of fresh and fourth-cycled sodium silicate catalysts. The two diffractograms were almost the same suggesting that there was no change in the crystal phase. To determine the base strength of the catalysts the authors performed CO_2-TPD measurements. It was noticed that in the high temperature region, the basicity of the fresh catalyst was reduced after four cycles, indicating the occurrence of leaching of strong basic species into methanol in reaction and washing processes.

Varisli et al. (Varisli et al., 2017), studied the production of hydrogen from ammonia in an microwave reactor with iron incorporated mesoporous carbon catalysts and compared the results with conventional heating. A microwave power between 600 and 900 W was used and the catalyst amount was 0.1 grams catalyst (5 to 15 % iron in mesoporous carbon). For the microwave assisted experiments, the conversion of ammonia started at 300 °C and over 60% conversion was achieved at 400 °C, while with the conventional system almost no activity was seen below 500 °C. Complete conversion occurred at 600 °C in the conventional reactor at 450 °C for microwave heating (with mesoporous carbon catalyst doped with 7.7 % iron). The authors also noticed higher efficiency for the microwave system and attributed it to higher heat transfer rates in microwave system because of the direct volumetric heating of the catalysts.

Xie et al. (Xie et al., 2014) tested microwave assisted gasification using metal oxide catalysts under various conditions and studied their effect on syngas production and tar removal. Their study used microwave power of 750 W for gasification of corn stover feedstock using Fe, Co and Ni with alumina support catalysts. The preferred metal loading was 15% on Al_2O_3 and was realized by wet impregnation. SiC (800 grams) was used as microwave absorbent. The study concluded that microwave heating is an efficient method for biomass gasification as gas yields over 65% were obtained for all conditions. Catalyst proved to be a required addition in the gasification experiments since all catalysts performed better than in the case of non-catalytic reactions. Ni/Al_2O_3 had a better catalytic effect compared to other catalysts with gas yields reaching above 80% and a tar content of about 7 %. However, the H_2 to CO ratio was low and hence steam was added to further experiments. In this new setup, a H_2 to CO ratio of 1.49 was obtained and the gas yield was augmented to almost 84% while the tar content was reduced to 2%. Another benefit of adding steam was that methane disappeared completely as it was converted to hydrogen and carbon monoxide.

Lahijani et al., (Lahijani et al., 2014) reported the CO_2 gasification of oil palm shell char under catalytic microwave irradiation. The effects of char particle size and used iron supported char catalyst (5% Fe $(NO_3)_3$ loaded on oil palm shell char) was investigated. Temperatures between 750 and 900 °C and CO_2 flow rate between 50 and 125 ml/min were used. The authors concluded that the catalyst proved to be very efficient in increasing the reaction centers and active sites on the char's surface and obtained a CO_2 conversion of 99 % compared to only 93 % when uncatalyzed char was used.

Dong et al. (Dong et al., 2017), studied the effect of Fe^{3+} on microwave assisted pyrolysis of moso bamboo using hydrofluoric acid washing to demineralize the biomass. The study used 800 watts microwave power (from 3600 W available) for 20 minutes, 30 grams feedstock (moso bamboo impregnated with $FeCl_3$ at various concentrations (0.01 up to 1%). Without catalyst, yields of 17.8 % solid, 35.1 % liquid and 47.1 % gas were obtained. With the use of catalyst, the gas yield increased to 51.9 wt%, 53.1 wt%, 60.7 wt% and 63.5 wt% with $FeCl_3$ concentration of 0.05, 0.1, 0.5 and 1 %, respectively, while the liquid yield decreased to 25-30%. Also, the concentration of CO_2 and CH_4 decreased while that of CO and H_2 increased with catalyst addition, this trend being accentuated by the concentration of $FeCl_3$. The study also found that $FeCl_3$ was transformed to Fe_2O_3 during microwave pyrolysis suggesting an interaction between Fe_2Cl_3 and CO.

Zhou et al., (Zhou et al., 2017) studied the decomposition of methylbenzene under microwave irradiation using iron supported zeolites. It was employed a 700 W microwave generator to obtain 300 °C. They used methylbenzene as a model compound for tar and ZSM-5 doped with Fe^0 as catalyst. For conventional heating the authors did not observe a decrease in methylbenzene concentration. However, under microwave heating the methylbenzene concentration decreases significantly over Fe^0/ZSM-5. They noticed that hydrogen was the first product observed along with some methane and solid carbon deposits.

While biomass catalytic gasification studies are limited using microwave heating, there are significant number of studies focusing on microwave assisted catalytic reforming of methane and carbon dioxide. Fidalgo et al., (Fidalgo et al., 2011) studied CO_2 reforming of CH_4 on Ni catalyst over Al_2O_3 using carbonaceous material (metallurgical coke and activated carbon) as microwave absorber at 800 C. They found that the carbonaceous materials acted as a catalyst in the CH_4 reforming reaction and a combination of activated carbon and Ni/Al_2O_3 was a better catalyst compared to coke-Ni/Al_2O_3 combination. They concluded that higher conversion to H_2 was achieved in microwave reactor compared to conventional heating.

Dominguez et al., (Dominguez et al., 2007) studied the effect of microwave heating on CH_4 conversion to H_2 in CO_2-free reforming reaction at 800 °C with activated carbon as catalyst. Since activated carbon readily heats in the microwave, microwave absorber was not used. The authors found that at 800°C, the methane conversion was higher using the microwave reactor compared to conventional reaction. However, as the temperature increased, this difference decreased steadily. In addition to successful methane conversion in microwave reactor, the authors also reported production of carbon nanofibers on activated carbon surface as a desirable byproduct. Another study using carbon based material (char) as absorber as well as catalyst was reported by the same group (Dominguez et al., (A. Dominguez, 2007)) for biogas dry reforming to syngas in a microwave heater. They studied the effect of potassium char obtained from biomass pyrolysis as catalyst for dry reforming of methane using CO_2. The study noted that microwave heating generates hot spots or microplasmas inside the catalyst bed, resulting in higher conversion of methane to H_2 compared to conventional electric heating reactor. One of the problems associated with this process was formation and deposition of coke on char surface. To address this issue, the authors mixed the CH_4 stream with CO_2, which partially removed the carbon deposits and prolonged catalyst life. Thus, the conversion of CO_2/CH_4 mixture to H_2 using potassium rich char provided an *in situ* route for catalyst regeneration within the process. Zhang et al., (Xunli Zhang, 2003) studied platinum based catalysts for methane reforming inside a microwave reactor. The catalysts tested were monometallic Pt/Al_2O_3 and support based $CeO_2/\gamma\text{-}Al_2O_3$ or $La_2O_3/\ \gamma\text{-}Al_2O_3$. The reforming reaction was carried out at temperatures between 450 – 800 °C. The authors found that the CO_2 and CH_4 conversions and H_2/CO product selectivity was higher for microwave based reactions when compared to conventional heater. This effect was attributed to hot spot formation inside the microwave reactor.

Another application of microwaves for gasification product reforming is use of microwave generated plasmas. Jasinksi et al., (Jasiński et al., 2008) studied the conversion of methane to hydrogen in microwave generated plasmas under atmospheric pressure, using nitrogen. They used Ni catalyst on alumina globules and compared the effect on methane conversion with and without catalyst. They noted that with the use of microwave plasma, the production rate of hydrogen increased (255 g[H_2]/h) as well as the energy efficiency (85 g[H_2] kWh^{-1}). Moreover, loss of oxygenated compounds was desirable. They concluded that this method would be cost effective and hence promising for methane reforming applications.

Microwave plasma was also tested for methane steam reforming in presence of Ni/Al_2O_3 catalyst by Wang et al. (Wang et al., 2010). They noted that while microwave plasmas certainly increased the H_2 product selectivity (95.2%) and elevated CH_4 conversion, intermediate products such as nano carbon powders, CO_x, C_2H_2, C_2H_4, and HCN were formed. One of the drawbacks of using this method was that high carbon powder was formed that deposited on catalyst surface, deactivating the catalyst.

In microwave assisted gasification experiments catalyst were generally used in various reforming reactions. All catalytic experiments had better results than non-catalytic tests. Carbon based catalyst were efficient in glycerol reforming (Fernández et al., 2010) or methane conversion and formed carbon nanofibers as by products in some cases (Dominguez et al., 2007). Generally, Ni/Al_2O_3 proved to be a reliable catalyst in methane reforming reactions and even in biomass gasification, resulting in high syngas production and low tar content (Xie et al., 2014).

4. Conclusions

We analyzed different types of catalysts used in microwave assisted pyrolysis and gasification. We presented the results of catalytic upgrading in *in situ* and *ex situ* reactors available in literature. general observation is that the use of catalysts is favorable in terms of product yields and quality. *In situ* catalytic upgrading is widely used because of simple experimental set up Their main disadvantage is harder recovery and higher deactivation rate *ex situ* catalytic upgrading requires complex experimental set-upBut the catalyst temperature can be independently controlled of biomass temperature for best outcome, catalyst recovery is facile, and has lower deactivation rate.

Note: E-supplementary data for this work can be found in e-version of this paper online

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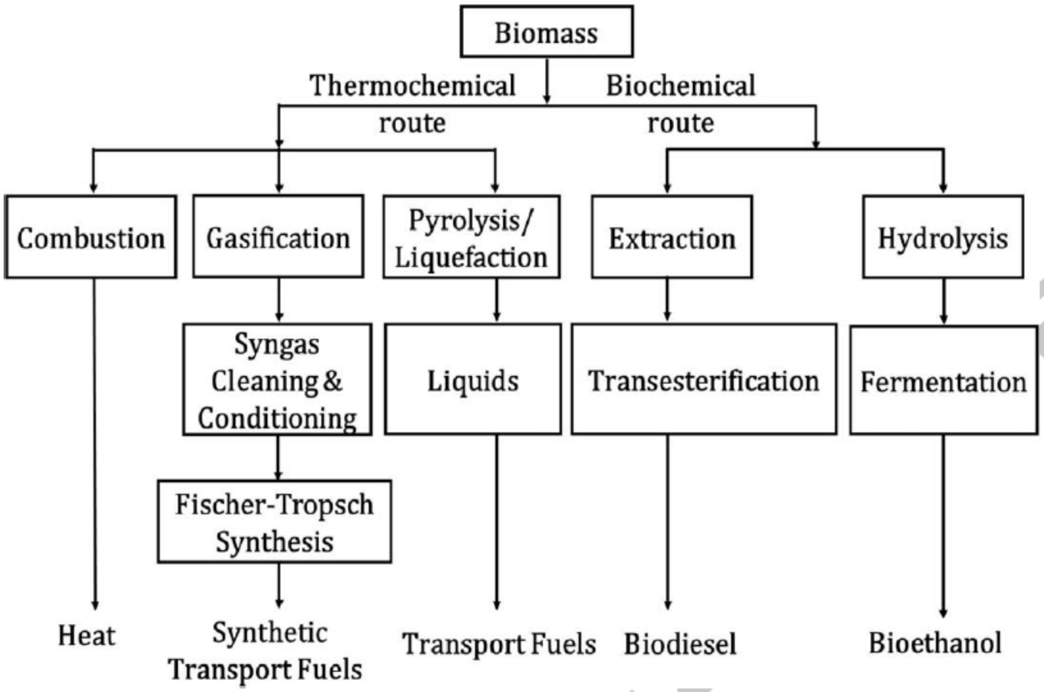
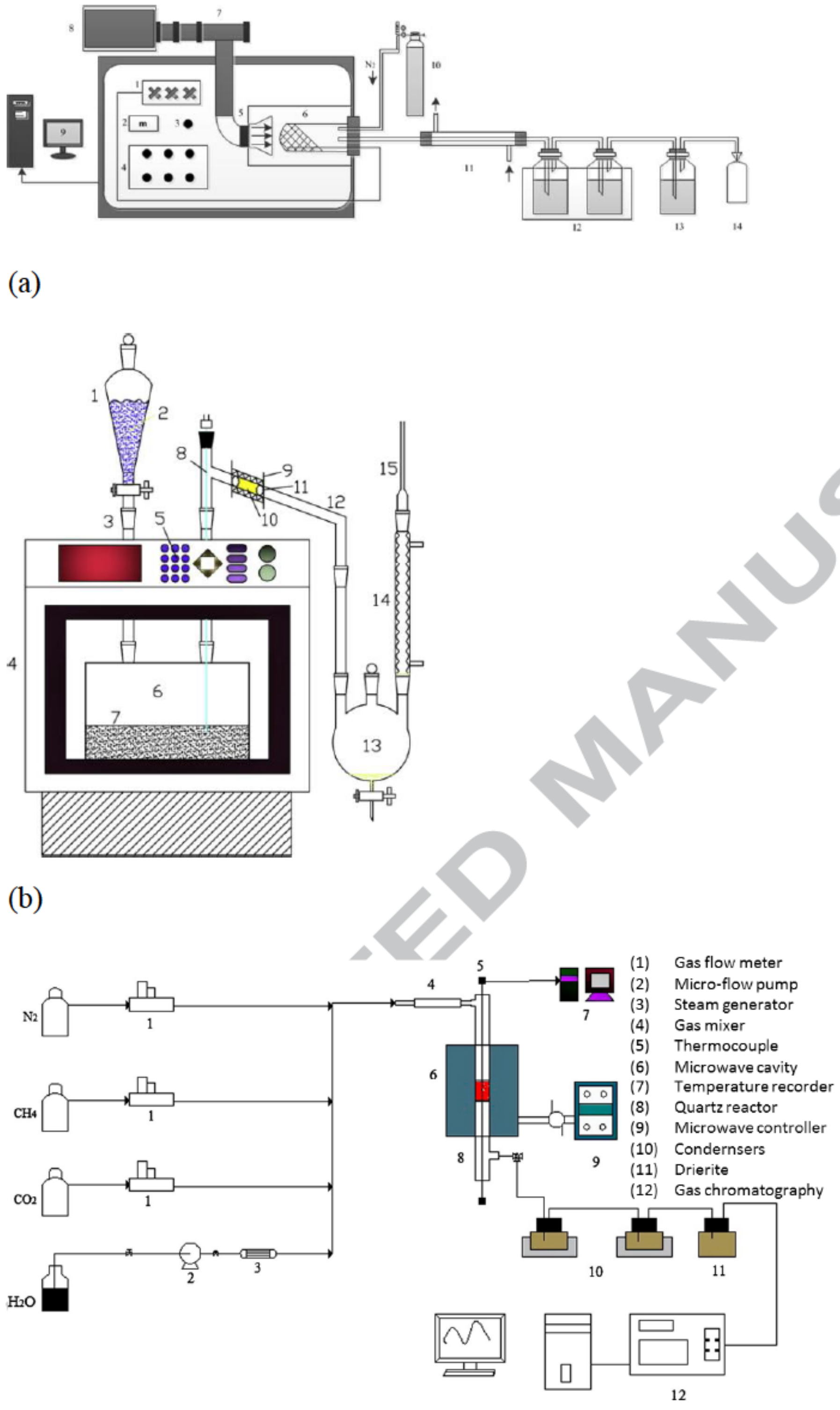


Figure 3. Thermochemical and biochemical pathways for conversion of biomass (Sikarwar et al., 2017)



(a)

(b)

(c)

Figure 2- Experimental set-up using microwave reactor for (a) in situ catalytic upgrading (Ma et al., 2017), (b) ex situ catalytic upgrading *(Liu et al., 2017) (c)* microwave assisted catalytic gasifier (Li et al., 2016)

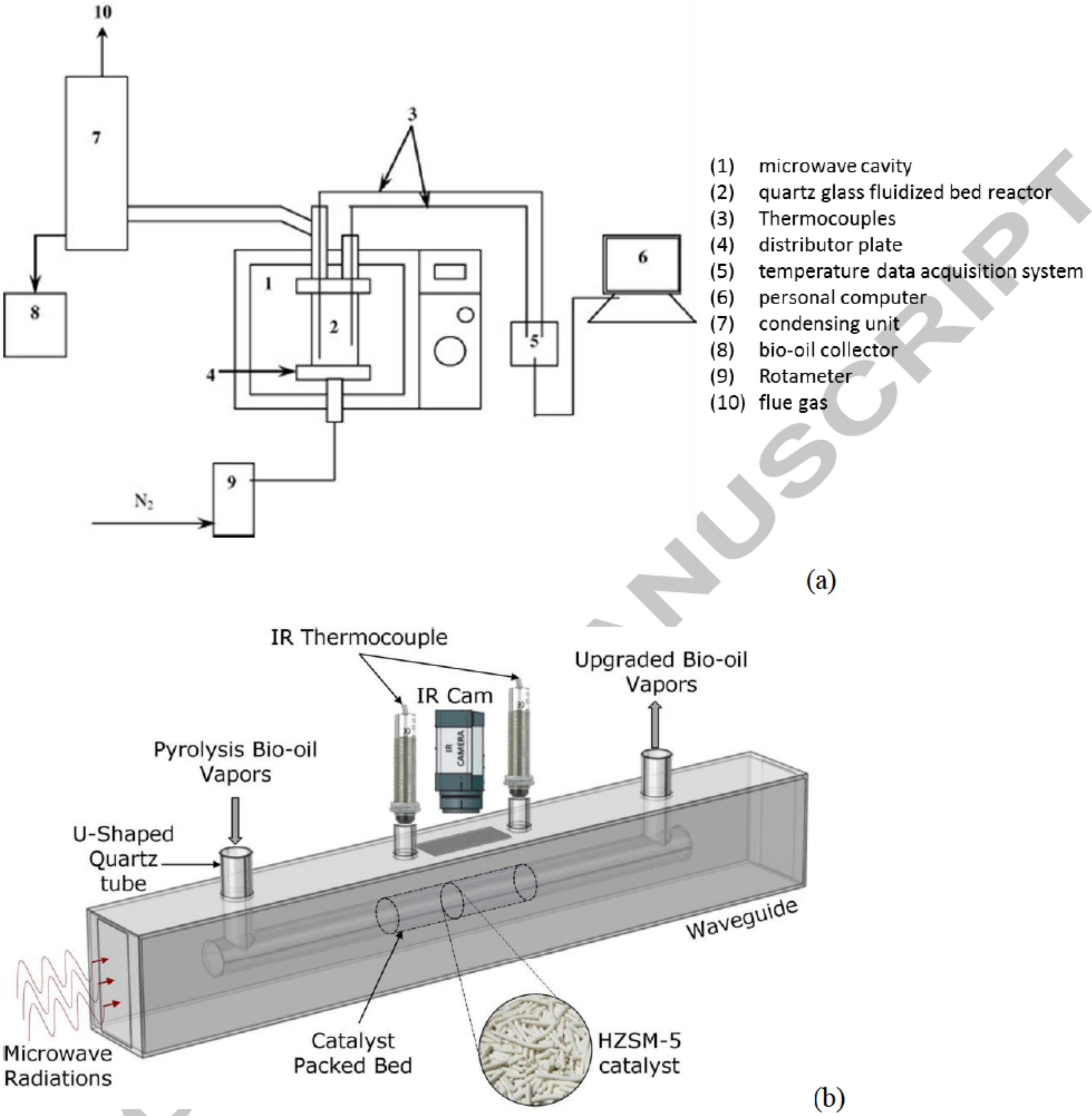
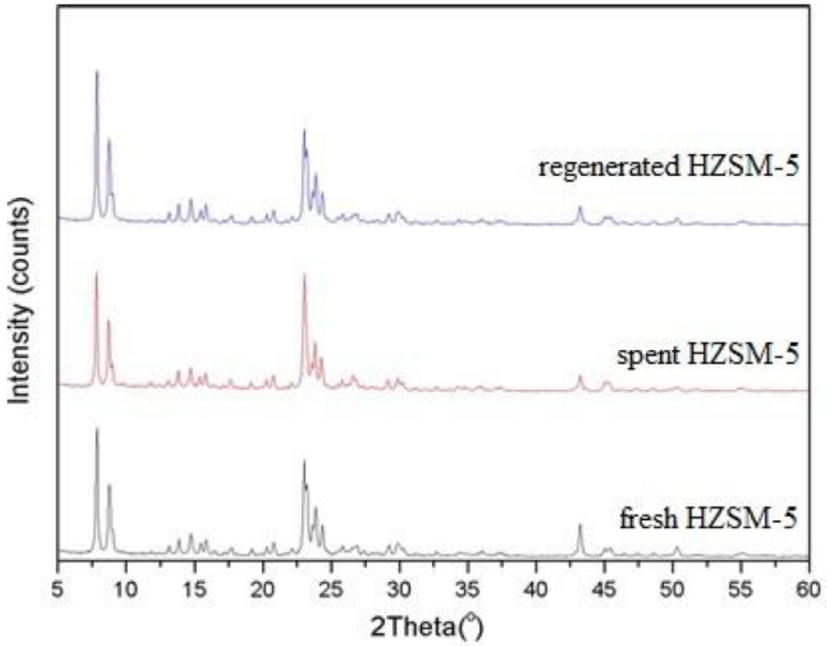
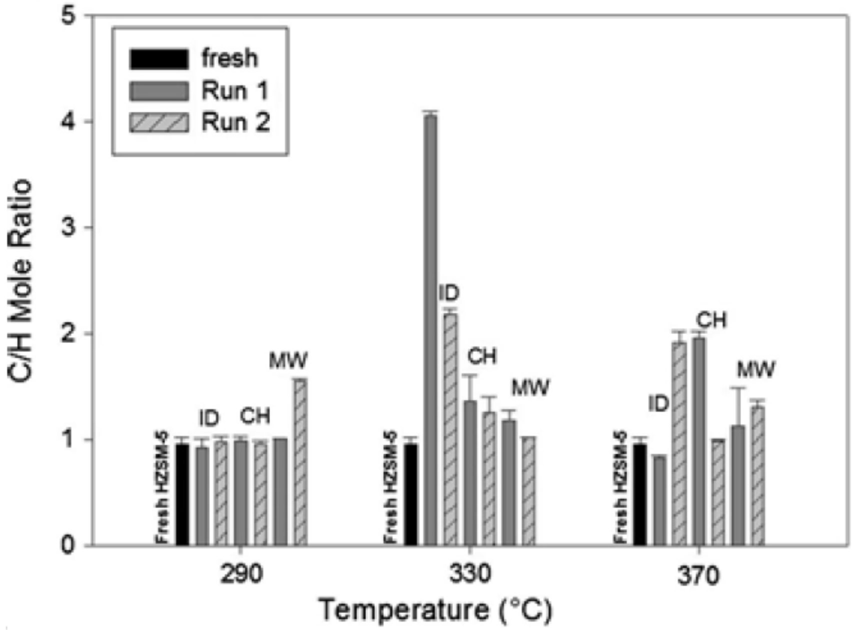


Figure 3. Microwave catalytic reactor (a) Fluidized bed (Salema & Ani, 2011) (b) Fixed bed (Muley et al., 2016)



(a)



(b)

Figure 4 – Catalyst characterization for (a) XRD patterns of fresh, spent and regenerated catalyst, for fresh HZSM-5, spent HZSM-5 and, regenerated HZSM-5 (Liu et al., 2017) and (b) C/H ration from elemental analysis for fresh and coked catalyst (Muley et al., 2016)

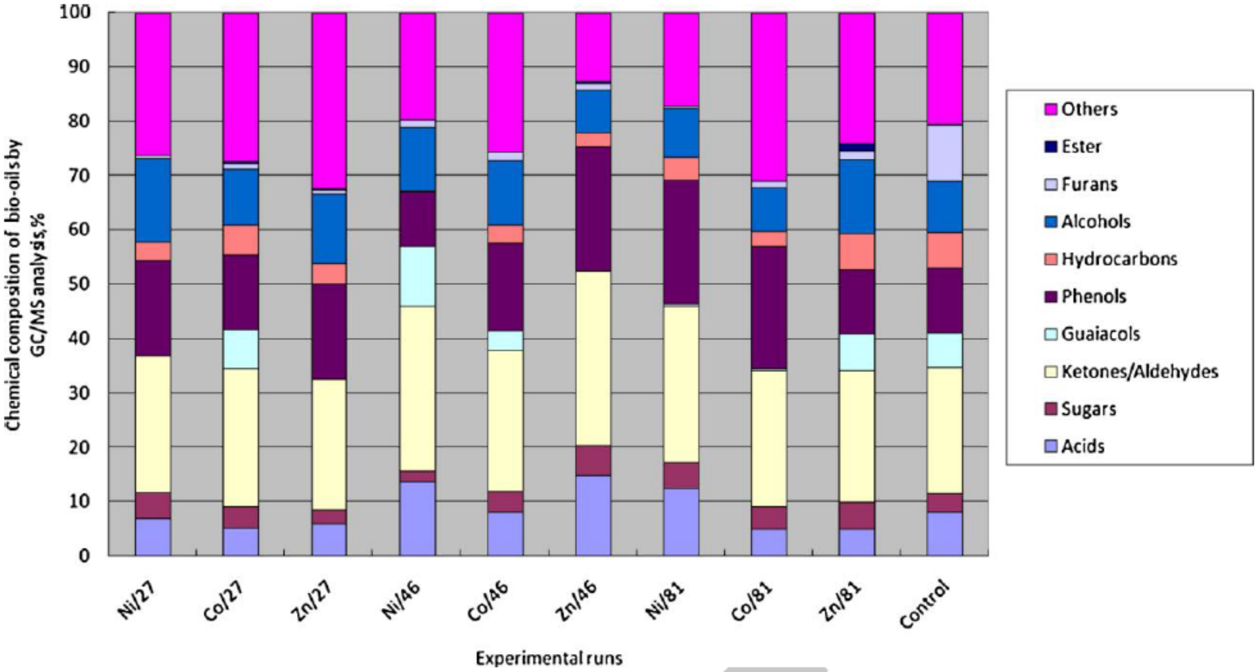


Figure 5 – GC analysis of chemical composition of bio-oil obtained with and without catalyst for modified ZSM-5 catalyst (Liang et al., 2017)

Table 1. Catalysts used in microwave assisted pyrolysis

Class	Type	Catalyst	Feedstock	MW power	Feedstock/ catalyst	Temp. pyrolysis ; catalyst bed	Observation	Ref.
Zeolites	in situ	EDTA modified HZSM-5	mushroom waste	750W	1:1	550°C	Decrease in liquid products and a significant increase in gases and water. higher selectivities towards sugars and alcohols, and lower selectivities towards low molecular oxygenated chemical compounds such as ketones, esters and phenols	(Wang et al., 2016)
	in situ	various	lignin			550-650°C	Higher temperatures favor the production of phenol and alkyl phenols while inhibiting the production of methoxylated phenols. The aromatization capacity of zeolites increases with the increasing acidity of both external and internal acidic sites, which increase with the decreasing ratio of Si/Al. HZSM-5 is the most effective catalyst for the production of deoxygenated compounds because of its stronger acidity.	(Fan et al., 2017b)
	in situ	HZSM-5	lignin and LDPE (low density polyethylene)	750W	1:2; 1:1; 2:1	450-600°C	HZSM-5 improved the production of aromatics.	(Fan et al., 2017a)
	ex situ	HZSM-5	corn stover	750W	5:1	450-600°C ; 425°C	Bio oil yield = 33.38 wt.% (and maximum proportion of aromatic compounds (26.20%). Potential industrial chemical compounds obtained from bio-oil at 550 °C included toluene (0.70%), xylene (3.73%), indene (5.14%), phenol (4.65%) and naphthalene (15.62%),	(Liu et al., 2017)
	ex situ	HZSM-5, SiO_2-HZSM-5	corn stover	750W	20:1	500°C; 500°C	A decrease in coke yield was observed when the SiO_2 deposited amount increased from 0% to 5.9%. The relative contents of aliphatic hydrocarbons, aromatic hydrocarbons and total hydrocarbons increased, and the relative content of oxygen-containing aliphatic compounds decreased with increasing SiO_2 deposited amount from 0% to 3.7%. The highest concentration of syngas (H_2 + CO) found was 32.94%, and it could be used as high quality fuel.	(Zhang et al., 2015a)
	ex situ	CoZSM-5, ZnZSM-5, NiZSM-5	rice straw	750W	20:1	500°C; 500°C	CoZSM - highest liquid yield. On average the addition of catalyst has a positive effect on bio-oil yield averaging about 25% increase. The concentrations of aldehydes/ketones and phenols increased significantly comparing with the control experiments.	(Liang et al., 2017)
	ex situ	HZSM5	lignin		10:1, 10:2, 10:3, 10:4	550°C 250-550°C	At higher catalyst:lignin ratios and 550 °C catalytic temperature lower bio-oil yield and higher gas yield was obtained. The same catalytic temperature and a catalyst lo lignin ratio of 0.3 was best for the conversion of methoxy phenols to alkyl phenols and aromatics and syngas formation.	(Fan et al., 2018)
	ex situ	ZSM-5 coatings on SiC foam	corn stover		up to 2:1	550°C 425°C	The best results were obtained in a composite catalyst bed configuration, with 41.5 % aromatics and just 1.6 % oxygen containing aliphatics, and almost 19% BTEX.	(Zhou et al., 2018)

	ex situ	FeZSM-5	methyl benzene	700W		300°C	Methylbenzene concentration decreased to a much greater extent over Fe^0/ZSM-5; a stable concentration of 50% of the original concentration was reached	(Zhou et al., 2017)
Metal oxides	in situ	CaO, $CaCO_3$, NiO, Ni_2O_3, γ-Al_2O_3, TiO_2	sewage sludge	700W	10:1		CaO - highest proportion of H_2, lowest proportion of CO_2, CH_4 decreased significantly. $CaCO_3$ – at low temperatures CH_4 yield was extremely low, at high temperatures CO_2 and CO increased and H_2 decreased. NiO, Ni_2O_3 - the combustible gas (H_2+ CO + CH_4) yield over 65% of the total gases. γ-Al_2O_3, TiO_2 – at low temperatures, no significant change vs. no catalyst. At high temperatures γ-Al_2O_3 results in an increase in the yields of CH_4 and H_2	(Yu et al., 2014)
	in situ	NiO, CuO, CaO, MgO	corn stover	500W	10:1-33:1	450-520°C	H_2, CH_4, CO, and CO_2 were all slightly lowered. Liquid products contained fewer aromatics having 3 to 4 rings and were mainly composed of phenol (11.96–35.80%) and methylnaphthalene (19.61–43.28%).	(Huang et al., 2013)
	in situ	NiO, CuO, CaO, MgO	sugarcane bagasse	500W	10:1-33:1	490-532°C	H_2, CH_4, CO, and CO_2 were all slightly modified. NiO or CaO can be helpful for the formation of syngas, CuO and MgO decreased the production of syngas. All catalysts decreased the production of CH_4. CaO or MgO increased the gaseous fraction, while NiO or CuO increased the liquid fraction.	(Kuan et al., 2013)
	in situ	CaO, Fe_2O_3	sludge		10:1	500-900°C	Bio-char yields at 900 °C were lower than without catalyst. CaO efficient to produce bio-gas while Fe_2O_3 for bio-oil. The best quality of bio-oil was obtained at 800 °C with CaO, while the maximum bio-gas production could both be catalyzed by CaO and Fe_2O_3 at 900 °C. CaO performed better in H2 production, while Fe_2O_3 was preferred for CH_4 production.	(Ma et al., 2017)
	in situ	Fe_3O_4, MnO_2, CoO,Co_3O_4, NiO, CuO	coal, biomass				Metallic oxides can serve as microwave absorbents. At microwave assisted pyrolysis of coal some metallic oxides can crack aliphatic and aromatic hydrocarbons in the order of Fe_3O_4, >Al_2O_3, >CaO>SiO_2, >quartz bead. Fe_3O_4 enhanced syngas (CO+H_2) yield.	(Mushtaq et al., 2014)
	in situ	MgO, Fe_2O_3, MnO_2, CaO, CuO	food waste	300-600W	20:1	up to 800°C	MgO and MnO_2 increased the maximum temperature and the average heating rate, CaO, CuO and Fe_2O_3 had the opposite effect. The yield of solid residue rose while the bio-oil and the gas yields decreased with CaO and CuO. MgO, Fe_2O_3 and CuO caused liquid yield to decrease and the gas to yield increase.	(Liu et al., 2014b)
	ex situ	MgO	LDPE (low density polyethylene)	3000W	15:1; 10:1; 5:1; 3:1	350-550°C; 350-550°C	Lower yield of liquid, the total percentage of gasoline fraction ranged from 79.5% (37.3% mono-aromatics and 42.2% C5-C12 aliphatics) to 96.0% (39.7% mono-aromatics and 56.3% C5- C12 aliphatics)	(Fan et al., 2017c)
Carbon	in situ	AC (activated carbon)	lignin	700W	1:1.5 up to 1:4.2	350-600°C	Bio-oil yield up to max 41.4% with AC (15% with no catalyst), gas yields up to a minimum of 10% with AC (55% with no catalyst), the char yields up to max 54% with catalyst (30% without catalyst)	(Bu et al., 2014)
	in situ	Ni/RHC, Fe/RHC, Cu/RHC (rice husk char)	rice husk	700W	3.3:1	up to 800°C	Gas yield was increased by all the tested catalysts while the liquid yield decreased. H_2 + CO was 69.96% maximum with the addition of Ni/RHC catalyst. Ni/RHC and Fe/RHC catalysts results in H_2/CO of 1.09 and 1.52	(Zhang et al., 2015b)

	in situ	AC (activated carbon), LC (lignite char)	palm kerne shell	2000W	10:1; 10:2	400-600°C	When AC and LC were used, very fast heating rates were achieved, LC showed higher heating rates than AC. The bio oil yield when AC was used was in the range of 23.30–29.58 wt.% and with LC ranged between 18.84 and 36.83 wt.%. The obtained bio-oil was also highly phenolic. With LC the phenol concentration in bio-oil ranged 2.24–2.89 mg/g, and with AC it ranged between 2.47–4.13 mg/g.	(Omoriyekomwan et al., 2016)
	in situ	AC, SiC, solid residue	Chlorella vulgaris (microalgae)	up to 2250W	20:1; 10:1; 5:1; 3.3:1	up to 750°C	Max bio-oil yield was 35.83 wt.% and max gas yield was 52.37%, achieved under 1500 W and 2250 W, respectively. Activated carbon exhibited the best catalytic activity followed by solid residue.	(Hu et al., 2012)
	in situ	AC supported iron III	moso bamboo	600 W	20:1; 10:1; 5:1; 2:1	up to 600 °C	The catalyst improved the content of syngas, reaching 81 vol%, with a H2/CO ratio of 1.04 and inhibited CH4 and CO2 production	(Dong et al., 2018b)

Table 2. Catalysts used in microwave assisted gasification

Type	Catalyst	Feedstock	MW power	Feedstock/catalyst	Temp. pyrolysis; catalyst bed	Observation	Ref.
ex situ	AC	glycerol reforming			800°C	Higher conversions of glycerol to gaseous products and higher H_2 and syngas yields compared to conventional heating. Carbon-based catalysts proved efficient for producing syngas with a H_2/CO ratio close to 1, while producing very small amounts of CO_2.	(Fernández et al., 2010)
ex situ	FeMC (iron incorporated mesoporous carbon)	ammonia decomposition			600-900°C	Conversion of ammonia started at 300 °C, over 60% was obtained at 400 °C, complete conversion was achieved at 450◦C (7.7 wt% Fe), while with conventional heating systems the conversion was achieved at 600 °C	(Varisli et al., 2017)
ex situ	Fe/char	CO2 gasification	1150W		750-900°C	CO_2 conversion increased from 93% in pristine char to 99% in Fe-catalyzed char	(Lahijani et al., 2014)
in situ	Fe-Al_2O_3, Ni-Al_2O_3, Co-Al_2O_3	corn stover	750W	3:1	900°C	All catalyst performed better than in the case without catalyst. Ni/Al_2O_3 is better than the other two catalysts. Gas yield reached above 80% while tar content was as low as 7% when using Ni-based catalyst. Ni/Al_2O_3 - the maximum syngas (H_2 + CO) yield was obtained	(Xie et al., 2014)
in situ	Ni/Al_2O_3 Activated C + Ni/Al_2O_3 Coke + Ni/Al_2O_3	Methane/ CO_2	-	-	800°C	Higher conversion to H_2 was achieved in microwave reactor compared to conventional heating.	(Fidalgo et al., 2011)
in situ	Activated Carbon	Methane	-	-	800°C	Higher conversion with microwave heating. Formation of carbon nanofibers as byproducts	(Dominguez et al., 2007)
in situ	Potassium char	Biogas (CH_4 and CO_2)	-	-	800°C	The conversion of CO2/CH4 mixture to H2 using potassium rich char provided an "in-situ" route for catalyst regeneration within the process	(A. Domingue z, 2007)
in situ	Pt/Al_2O_3 CeO_2/γ-Al_2O_3 and La_2O_3/ γ-Al_2O_3	Methane and CO2	50 W	-	450 – 800°C	The CO2 and CH4 conversions and H2/CO product selectivity was higher for microwave based reactions when compared to conventional heater. This effect was attributed to hot spot formation inside the microwave reactor.	(Xunli Zhang, 2003)
in situ	Ni on Alumina globules	Methane	3 – 5 kW	-	>800°C	The production rate of hydrogen increased (255 g[H2]/h) as well as the energy efficiency increased (85 g[H2] kWh-1). No oxygenated compounds were formed	(Jasiński et al., 2008)
ex situ	Ni/Al2O3	Methane	1 kW	-	750 °C	Microwave plasmas certainly increased the H2 product selectivity (95.2%) and elevated CH4 conversion, intermediate products such as Nano carbon powders, COx, C2H2, C2H4, and HCN were formed	(Wang et al., 2010)

Highlights

- I*n-situ* microwave catalytic process is frequently used due to simpler set-up
- *Ex-situ* microwave processes can lead to optimum temperatures and better results
- *Ex-situ* process has low deactivation rates *in situ* catalysts deactivate easily
- Catalytic microwave-assisted process is favorable for yields and product quality
- Commonly used catalysts: zeolites, metal oxides, various salts and carbon materials