Catalytic Effect of $CaCl_2$ and $ZnSO_4$ on the Pyrolysis of Cedar Sawdust

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The catalytic pyrolysis of biomass is a promising way to improve Bio-oil properties and increase the selectivity to targeted chemicals. The catalytic effect of $ZnSO_4$ and $CaCl_2$ on the pyrolysis of cedar sawdust was studied via simultaneous thermogravimetric analysis and mass spectrometry (TG/MS). 3% of each catalyst and a mixture of 1.5% of each one were added to cedar biomass samples. Experiments were performed in helium atmosphere at 100 K/min. Kinetics was evaluated using two models: *nth* reaction order model, and distributed activation energy model (DAEM). Catalyst had a strong influence on the distribution of major products and the thermogravimetric profile of the pyrolysis process. Thermogravimetric data had a good adjustment to DAEM model. Both catalysts speed up the pyrolysis of cedar sawdust and have a strong influence on kinetics parameters of pyrolysis of the studied biomass.

1. Introduction

Sustainable generation of heat and power from biomass is the object of study of many research works worldwide, due to the decreasing availability of fossil fuels and the increase of people awareness and concern about the adverse effects of contaminants generated by conventional power systems (Di Blasi, 2008). Pyrolysis is one potential route for the thermochemical transformation of biomass in chemical commodities. Pyrolysis products are classified in gases, tar, and char (Balat et al., 2009).

Most studies, using several kinds of biomass, show that the obtained bio-oil has not enough quality to be used directly in combustion engines, and it must be upgraded, raising production costs. One option to lower upgrading associate costs is catalytic pyrolysis which has been reported to improve bio-oil, but also has a lower yield of liquid products, for most of the studied catalysts. Recent studies have shown that use of mixed catalysts can improve bio-oil properties (Zhang et al., 2013a).

The first and obvious application of pyrolysis volatiles is as fuels; however production of fuels is not the sole potential application field of biomass pyrolysis due to many organics functionalized compounds that can be produced which can become precursors of chemicals of high added value (Balat et al., 2009, Zhang et al., 2013b). From this point of view, the use of catalysts for biomass pyrolysis could have some advantages, such as the improvement of obtained fuels, increased yields of either the main product or a particular chemical. Several catalysts have been employed to improve quality parameters of pyrolysis products: oxides, salts, and hydroxides of metals; zeolites; micro-, meso-, and macro-porous catalysts, and even minerals naturally occurring in biomass (Zhang et al., 2013a, Yang et al., 2006).

Other studies have targeted valuable chemical compounds from biomass pyrolysis using catalysts such as silicates, molybdenum and cobalt oxides, sulfuric acid, sodium hydroxide, ferric sulfate (Chen et al., 2011), and zinc chloride(Rutkowski, 2009), obtaining different product distributions for each catalyst. Ferric sulfate improves bio-oil yield, increase CO and decrease CO_2 fraction in the gas phase, for tobacco stem pyrolysis (Chen et al., 2011). Zinc chloride has a similar effect on bio-oil yield and additionally change products proportions of pyrolysis of biomass-plastic blends (Rutkowski, 2009). Zn, Fe, and Cu supported on alumina

were used to upgrade bio-oil obtained from cedar; an increase in the content of monocyclic aromatics was obtained using Fe and Zn catalysts(Karnjanakom et al., 2015). Al-MCM-41, Fe–Al-MCM-41, Cu–Al-MCM-41, and Zn–Al-MCM-41 showed an improvement of bio-oil properties(Nilsen et al., 2007). Calcium oxide was used in the catalytic pyrolysis of forest pine woodchips; it was found that bio-oil acidity was lowered, as a consequence of dehydration reactions promoted by the catalyst(Veses et al., 2014). Mixtures of micro- and meso-porous catalysts have been employed to obtain upgraded bio-oil, but also lower yields (Zhang et al., 2013a). In this work, the catalytic effect of $ZnSO_4$ and $CaCl_2$ on the pyrolysis of cedar sawdust, a common and widely available by-product of the wood industry, was evaluated. Thermogravimetric analysis was employed in order to evaluate the effect of catalysts on char yield, pyrolysis temperature, and kinetics parameters of pyrolysis reaction.The obtained results allowed evaluating the potential of the studied catalysts in the catalytic pyrolysis of cedar biomass.

2. Methodology

2.1 Materials

Cedar sawdust was obtained from a local carpentry of Barranquilla, Colombia. Sample was grinded and sieved, and the fraction with particle diameter lower than 100 μm was used in experimental tests. $ZnSO_4 \cdot 7H_2O$and $CaCl_2 \cdot 2H_2O$were supplied by Sigma- Aldrich.

2.2 Sample preparation

Impregnation of cedar sawdust with Zn and Ca was done stirring for two hours 1.00 g of biomass with 14 ml of the impregnation solution. Impregnation solutions were prepared adding the required amount of either zinc sulfate, or calcium chloride, or both to achieve a final metal concentration of 3 % w/w. After impregnation, samples were dried at 80 C for two hours and additional two hours at 105 C and later stored in desiccator until use.

2.3 Thermogravimetric analysis

Thermogravimetric analysis was performed using a Thermogravimetric Analyzer TA instruments with lower detection limit of 0.1 μg. Control and acquisition of experimental data were made by Universal Analysis software. Linear ramps of 10, 30 and 100 K/min were employed. Purge of the gases was made with helium 5.0.

2.4 *n*th reaction model

In this model, the reaction rate can be expressed as a function of a temperature-dependent rate constant and a conversion-dependent function. The temperature dependence of the rate constant with temperature follows the Arrhenius equation, and the form of the reaction function is a nth reaction model, hence the equation that describes the volatilization rate can be written as Eq(1):

$$\frac{d\alpha}{dt} = Ae^{-\frac{E}{RT}}(1-\alpha)^n \tag{1}$$

Where *A* is the pre-exponential factor, *E* is the activation energy, *n* is the reaction order, and *α* is the conversion, defined as (Bungay, 2017):

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \tag{2}$$

m_0 and m_f are the initial and final mass of the decomposition process, respectively. m_t is the mass of the sample at any time *t*. Introducing the heating rate β, the previous equation can be expressed as Eq(3):

$$\frac{d\alpha}{dT} = \frac{A}{\beta}e^{-\frac{E}{RT}}(1-\alpha)^n \tag{3}$$

Eq(3) can be linearized in Eq(4) and kinetics parameters obtained from the fitting of experimental data to it (Açıkalın, 2012).

$$\ln\left(\frac{d\alpha}{dT}\right) - n\ln(1-\alpha) = \ln\left(\frac{A}{\beta}\right) - \frac{E}{RT} \tag{4}$$

2.5 Distributed activation energy model (DAEM)

DAEM uses the assumption that a set of irreversible parallel first order reactions occurs, characterized for a continuous distribution of activation energy that can be represented by a distribution function $D_j(E)$ (Chen et al., 2016, Cheng et al., 2015).In this model, the first derivate of a thermogravimetric curve (DTG) is calculated with Eq(5):

$$Y^{calc}(t) = -\sum_{j=1}^{M} c_j \frac{dx_j}{dt} \tag{5}$$

where Y^{calc} represents the conversion rate of the sample; M is the number of reactions or pseudo components of the sample; c_j is a proportionality constant, and dx_j/dt is the rate of consumption of the pseudo-component j (Varhegyi et al., 1997, Várhegyi et al., 2009, Várhegyi et al., 1998), which can be calculated as:

$$\frac{dx_j}{dt}(t) = \frac{1}{2\sqrt{\pi}} \int_{-\infty}^{\infty} \exp[\mu_j{}^2] \exp[0,75\mu_j{}^2] \frac{dX_j(t,\mu_j)}{dt} d\mu_j \tag{6}$$

Where $\mu_j = 2(E - E_{0j})/(\sqrt{2}\sigma_j)$ y $X_j(t,\mu_j)$ is the solution for dx_j/dt at t time and the value of the energy of activation E. Solution of Eq(6) was found using Matlab software as described previously (Albis et al., 2013).

3. Results

Figure 1 shows TG and DTG curves for cedar sawdust with and without catalysts, heated at 100 K/min. The obtained TG and DTG curves are typical for biomass pyrolysis. From figure 1 is clear that both catalysts have a strong influence on TG and DTG profiles. Ca catalyst and combined Zn and Ca catalysts increase char fraction, whereas Zn catalyst decreased char content if compared with the cedar sawdust pyrolysis without catalyst (Table 1). Zn also has a more pronounced effect on peak temperature, shifting the pyrolysis main event to lower temperatures. Ca also lower the pyrolysis temperature but to a lower extent than Zn. The effect of the combined catalyst is to decrease pyrolysis temperature but to a lower extent that both sole catalysts. Experimental cedar TG and DTG profiles agree with thermograms reported in literature (Ota and Mozammel, 2003).
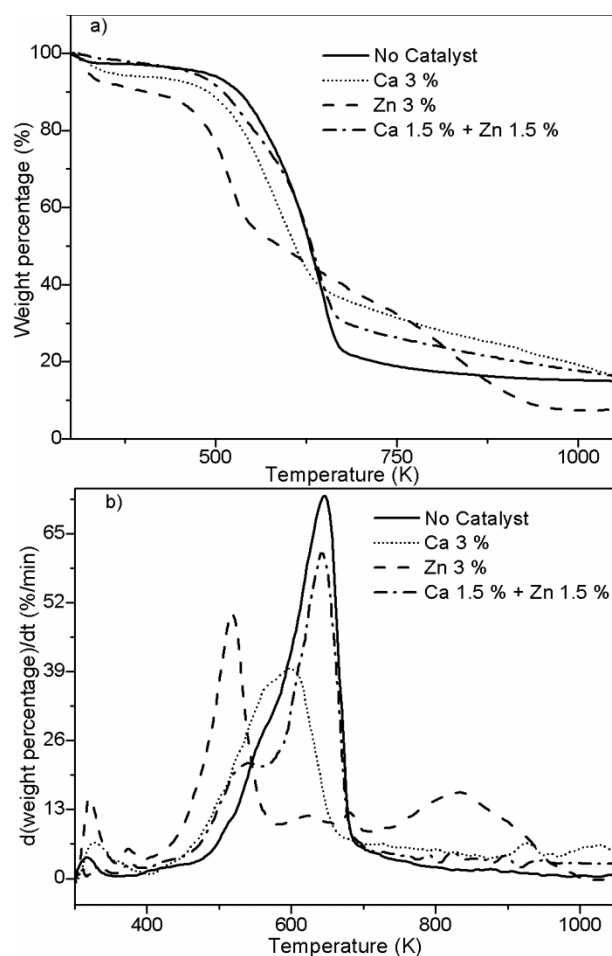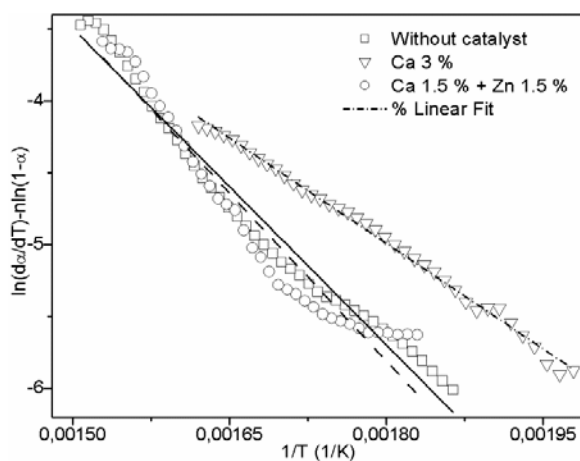

Figure 1: TG and DTG thermograms of cedar sawdust with and without catalysts. Heating rate is 100 K/min.

Table 1: Effect of catalysts on char yields, pyrolysis peak temperature and pyrolysis temperature range.

Sample	Peak Temperature (K)	Temperature range of pyrolysis (K)	Char (%)
Cedar Sawdust	647.21	387-873	15.2
Cedar Sawdust + $CaCl_2$	595.17	403-873	20.5
Cedar Sawdust + $ZnSO_4$	516.37	393-583	7.6
Cedar Sawdust +$ZnSO_4$ + $CaCl_2$	639.15	423-713	18.4

3.1 *n*th reaction model

Fitting of experimental data to the nth reaction model is shown in Figure 2 and fitted parameters are shown in Table 2. Data of cedar sawdust pyrolysis without catalysts, with 3 % Ca catalyst, and with 1.5 % Ca + 1.5 % Zn fit well to the *n*th reaction model with R^2 close to one, reaction order of 0.76 and activation energies ranged between 30,000 and 60,000 J/mol. The obtained reaction order is close to the one reported by (Ota and Mozammel, 2003) (0.71), but activation energies are higher than the reported by the same authors (7,540 J/mol). The fitting of data of the pyrolysis of cedar sawdust catalyzed with Zn showed reaction order, pre-exponential factor, and activation energies excessively high, hence obtained kinetics parameters are not reliable. Both Ca, and the mixture of Ca and Zn catalysts lower the activation energy of the process, which explain the lower pyrolysis temperatures when these elements are present.

Figure 2: Fitting to nth reaction model.

Table 2: Fitting of experimental data to nth reaction model

Sample	Reaction order	Activation Energy (J/mol)	Pre-exponential factor (1/s)	R^2
Cedar Sawdust	0.76	60,865	3975.6	0.972
Cedar Sawdust + $CaCl_2$	0.76	40,702	76.2	0.995
Cedar Sawdust + $ZnSO_4$	>15	317,716	3.2E+33	0.985
Cedar Sawdust +$ZnSO_4$ + $CaCl_2$	0.76	32,261	7.29	0.939

3.2 Distributed activation energy model (DAEM)

In Figure 3, the fitting of experimental data to DAEM model with three pseudo-components is observed. Fitting data is presented in Table 3.

Kinetics parameters are in the range reported for other biomass (Albis et al., 2013, Cai et al., 2014). Zn catalyst has the most influence on cedar sawdust pyrolysis parameters, which is observed in lower activation energies, mainly for the first and second pseudo-components. The influence of Ca on kinetics parameters of first and second pseudo-components is less marked than in the case of pyrolysis using Zn catalyst, but even then it is observed a slight lowering of the activation energy for these pseudo-components. However, the

presence of Ca increases the activation energy of the pyrolysis of the third pseudo-component, which can be interpreted as a retardant effect of the pyrolysis of this component. Finally, the combined use of Ca and Zn catalysts shows no effect on the pyrolysis of the first pseudo-component; there is a slight decrease on the activation energy of the second pseudo-component and an increase in the activation energy of the third pseudo-component. The effect of Zn is predominant for the first pseudo-component, and the effect of Ca is prevailing on the third pseudo-component. No synergistic effects were observed for Ca and Zn catalysts.
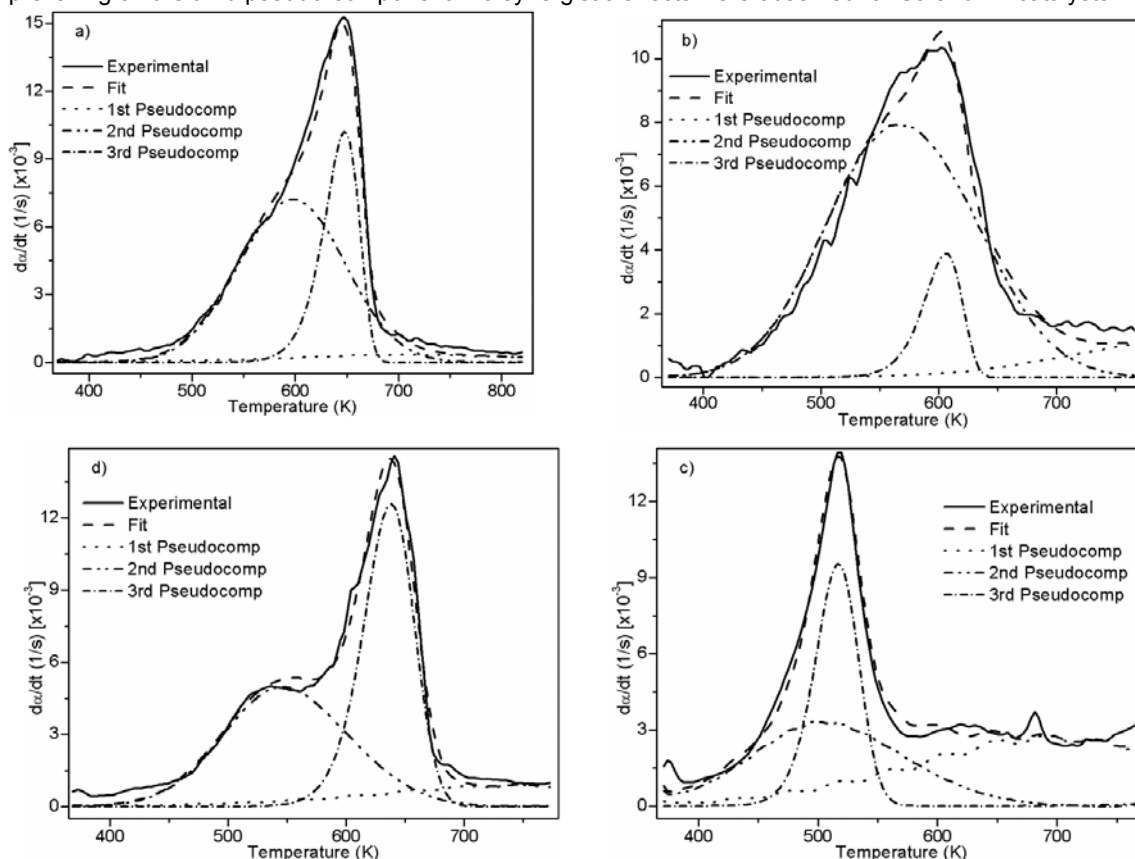

Figure 3: Fitting of DAEM with three pseudocomponents to DTG thermograms of catalytic and no-catalytic pyrolysis of cedar sawdust: a)no catalyser; b) $CaCl_2$ 3 %; c) $ZnSO_4$ 3% d) $CaCl_2$ 1.5 % + $ZnSO_4$ 1.5 %

Table 3: DAEM parameters with 3 pseudocomponents for catalytic and no-catalytic pyrolysis of cedar sawdust

Parameter	Cedar Sawdust	Cedar Sawdust + $CaCl_2$	Cedar Sawdust + $ZnSO_4$	Cedar Sawdust + $ZnSO_4$ + $CaCl_2$
c_1	5.60E-01	2.17E-01	5.74E-01	8.75E-01
A_1 (s^{-1})	3.41E+15	3.41E+15	3.41E+15	3.41E+15
E_{01} (J/mol)	2.05E+05	1.92E+05	1.64E+05	2.03E+05
σ_1 (J/mol)	3.05E+01	1.58E+03	7.63E+03	7.91E+03
c_2	1.20E+00	1.63E+00	6.55E-01	8.53E-01
A_2 (s^{-1})	2.30E+13	2.30E+13	2.30E+13	2.30E+13
E_{02} (J/mol)	1.67E+05	1.60E+05	1.43E+05	1.55E+05
σ_2 (J/mol)	2.63E+04	3.29E+04	3.54E+04	2.81E+04
c_3	1.19E-01	3.71E-01	9.70E-01	3.32E-01
A_3 (s^{-1})	5.36E+11	5.36E+11	5.36E+11	5.36E+11
E_{03} (J/mol)	1.77E+05	2.06E+05	1.73E+05	1.88E+05
σ_3 (J/mol)	6.03E+04	5.26E+04	6.03E+04	6.48E+04

4. Conclusions

It was shown that $ZnSO_4$ and $CaCl_2$ catalyse the pyrolysis of cedar sawdust. Ca and Zn lower the pyrolysis temperature of cedar sawdust, having Zn a more pronounced effect. Pyrolysis was successfully modelled using DAEM with three pseudo-components. Results showed that Zn and Ca have different effects on the pyrolysis of each pseudo-component of cedar biomass. Zn has a marked catalytic effect on first and second pseudo-components and Ca a retardant effect on the third pseudo-component.

Acknowledgments

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