

CATALYTIC PYROLYSIS OF WHEAT STRAW IN THE PRESENCE OF INEXPENSIVE CALCIUM - BASED CATALYSTS BY USING TGA-FTIR METHOD

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Abstract

Catalytic pyrolysis has been widely used as a convenient method for the direct conversion of biomass into liquid bio-fuels. Pyrolysis of wheat straw with or without catalysts was investigated using TGA-FTIR method in order to determine the influence of CaO, CaCO₃, Ca(OH)₂, and calcined dolomite catalysts on the evolution profile and relative yield of the volatile compounds. All catalysts, except Ca(OH)₂, decreased the volatile matter and increased the solid residue of wheat straw. All catalysts promoted formation of olefins whereas CaCO₃ advanced formation of aromatics.

Key words: *wheat straw, catalytic pyrolysis, TGA-FTIR method, calcium-based catalysts*

1. INTRODUCTION

The development of alternative energy processes has become imperative due to concerns about the depletion of petroleum resources, emission of greenhouse gases, environment and climate changes. Lignocellulosic biomass is an abundant and renewable source that can be converted into fuel and chemical feedstocks (Hwang 2015). The conversion of biomass can be achieved in biological (fermentation and anaerobic digestion) or thermochemical (gasification, liquefaction and pyrolysis) processes. Among these conversion processes, pyrolysis is considered to be one of the most promising technologies for liquid oil (bio-oil) production, with solid char and non-condensable gases as valuable by-products (Wang 2010).

The composition of bio-oil is very complex and entirely different from the composition of petroleum fuels, usually consisting mixture of acids, ketones, aldehydes, phenols, sugars, hydrocarbons, and water. Bio-oil has some negative properties such as high viscosity, poor heating value, corrosiveness, and instability. This creates a significant economic barrier for production transportation fuel by pyrolysis process (Lazdovica 2016).

Catalytic pyrolysis has been widely used as a convenient method for the direct conversion of biomass into high quality liquid bio-fuels. Zeolites (ZSM-5; HZSM-5) have been known as usable catalysts for direct conversion of biomass-derived carbohydrates into aromatics and light olefins, but many problems were encountered, such as fast deactivation of the catalysts by coke deposition and formation of polycyclic aromatic hydrocarbons (Lazdovica 2016).

CaO is usually used as tar cracking catalyst in gasification (Wang 2010). Authors Zhao (2014) investigated the catalytic pyrolysis of sawdust with CaO and found that the CaO increased formation of hydrogen, methane and decreased formation of compounds containing carbonyl and carboxyl group, aromatic hydrocarbons. Veses (2014) studied catalytic pyrolysis of wood biomass in the presence of calcined calcite, calcined dolomite and found that both catalysts decreased oxygen content and acidity, and increased pH and calorific value. Case (2015) confirmed that calcium compounds catalyze deoxygenation in the form of dehydroxylation.

Analytical pyrolysis are valuable techniques to characterize biomass thermal conversion by combining pyrolysis with gas chromatography/mass spectrometry (Py-GC/MS) or by using thermogravimetric analyzer coupled with Fourier transform infrared spectrometer (TGA-FTIR). K. Lazdovica et al. studied intermediate and fast pyrolysis of buckwheat and wheat straws by using TGA-FTIR and Py-GC/FTIR (Lazdovica 2017). The influence of zeolites and noble – metals on pyrolysis of wheat straw and bran (Lazdovica 2015, Lazdovica 2016) and CaO and MCM-41 on pyrolysis of corncob (Wang 2010) were also studied by using TGA-FTIR.

The cultivation of grain is a dominant industry of agriculture in Latvia. The total production of grain reached 3.0 million tonnes in the year 2015 of which wheat amount reached 1.5 million tonnes. The wheat straw is residue of harvest which usually are being plowed into the ground as fertilizer (Lazdovica 2017). Thereby a wheat straw has been chosen for further study with idea of production of bio-oil as feedstock for biofuels and chemicals.

In this study, the catalytic effect of calcium-based catalysts (CaO, Ca(OH)₂, CaCO₃ and calcined dolomite) on the pyrolysis of wheat straw were studied. Investigation focuses on composition of volatile compounds. Composition of biochar and coke was not investigated.

2. MATERIALS AND METHODS

2.1. Materials

Raw material of wheat straw (WS) has been taken from Cooperative society of agricultural services „LATRAPs”. The biomass sample was dried at 105 °C for 24 h, then milled in a IKA A11 Basic mill, and completed by sifting through sieves with a wire mesh size of <3.15 mm. In the experiments mean fraction of biomass with particles size of 0.15-0.25 mm was used. The study involves the full characterisation of raw materials by the proximate, ultimate and composition analysis and determination of the higher heating value (HHV) (see Table 1).

Table 1. The proximate, ultimate and composition analysis and HHV of WS.

Proximate analysis (wt.%) ^a		Ultimate analysis (wt.%) ^a		Composition analysis (wt.%) ^a	
Volatile matter	73.7	Carbon	44.87	Cellulose	45.1
Fixed Carbon	21.2	Hydrogen	5.74	Hemicellulose ^c	30.2
Ash content	5.1	Nitrogen	0.36	Lignin	17.3
HHV, J/g ^a	17 658	Sulphur	0.24	Fat	1.1
Relative moisture (wt.%)	9.1	Oxygen ^b	43.69	Extractives	1.2

^aDry biomass

^bCalculated by difference: O(wt.%) = 100% - (C%+H%+N%+S%)- Ash%

^cCalculated by difference: Hemicellulose (wt.%) = 100%-cellulose%-lignin-fat%-extractives%-ash%

2.2. Catalysts

Calcium-based catalysts (CaO, Ca(OH)₂, CaCO₃) used in this study were purchased from Sigma – Aldrich with > 99.5% purity. Calcined dolomite used in this work was obtained by calcination of the Latvian dolomite (~28% CaO, 18% MgO, 5% Al₂O₃, 0,6% Fe₂O₃) from SIA “Jēkabpils dolomīts” at 900 °C for 3 h in muffle furnace. All catalysts were dried for 5 h at 105 °C and stored in a desiccator before using in pyrolysis experiments. In our case, the regeneration of catalysts was not performed.

2.3. TGA-FTIR experiments

Thermogravimetric analyzer (PerkinElmer STA 6000) is coupled with the Fourier transform infrared spectrometer (PerkinElmer Spectrum 100) by a transfer line (TL8000) to simultaneous investigation the mass loss of WS and formation of volatile products. Transfer line and gas cell are heated and maintained at an internal temperature of 230 °C to avoid condensation or adsorption of semi-volatile products during the thermal degradation process of biomass. The FTIR spectrum is recorded every 9 s in the spectral range between 4000 and 650 cm⁻¹ with resolution factor of 4 cm⁻¹. Dry biomass samples were heated from 30 up to 700 °C with heating rate of 100 °C/min and held for 10 min in a pure nitrogen flow of 20 ml/min supervised by a mass-flow controller. The mass of sample consists of 32 mg WS and 32 mg

catalyst. In the non-catalytic experiments biomass sample was mixed with quartz sand. Each experiment was repeated three times.

2.4. Determination of chemical composition of biomass

Identification of main volatile products of WS pyrolysis was performed by TG-FTIR method and Spectrum Search Plus database library. The characteristic absorptions of the volatiles used to ascertain their formation in WS pyrolysis process are listed in Table 2.

Table 2. The characteristic IR spectra absorptions of the volatiles.

Reference	Absorption band (cm ⁻¹)	Peak (cm ⁻¹)	Assignment	Compounds
(Lazdovica 2015, Lazdovica 2016, Lazdovica 2017)	2217-2391	2309	ν _{as} C=O	CO ₂
	2071-2207	2182	νC-O	CO
	2972-3018	3014	νC-H	CH ₄
	1690-1800	1771	νC=O	Organic Acids
	1700-1740	1738	νC=O	Ketones
	2770-2860, 1684-1745	1702	νC=O	Aldehydes
	3600-4000	3755	νO-H	H ₂ O
	3585-3650, 1058-1131	1062	νC-O-H	Alcohols, LG (levoglucosan), Xylosan
	1495-1513	1508	νC=C-OH	Phenols
	650-900	742,9	γC-H	Aromatics
	728-770 (phenyl) 735-770 (ortho)	720	γC-H	Toluene
	950-993, 900-920 (vinyl)	950	γ=CH ₂	Olefins

ν - stretching vibrations, ν_{as} – asymmetric stretching vibrations, γ - out-of plane bending

2.5. Volatile matter of biomass

The yield of volatile matter of WS received in catalytic pyrolysis process and amount of solid residue is calculated from the weight basis of TG data according to Eq. (1) and solid residue according to Eq. (2):

$$\text{Volatile matter} = 2 \frac{m_s - m}{m} * 100\% \quad (1)$$

where m_s – mass of sample (biomass and catalyst or quartz sand), g

m – mass solid residue (fixed carbon, ash, and catalyst or quartz sand), g

$$\text{Solid residue (\%)} = 100\% - \text{volatile matter \%} \quad (2)$$

2.6. The relative yield of the volatile compounds

The typical output from TG-FTIR instrument is IR spectra as a function of time, that pre-programmed on temperature shows three-dimensional (3D) absorbance stack plot obtained from volatile compounds of WS thermal decomposition in inert atmosphere. During the process of pyrolysis all acquired TG-FTIR data are gathered and subsequently can be used for obtaining absorption spectra profile over the temperature range for each of the corresponding volatiles. In this study relative yield for each compound is assumed as an integral intensity of absorbance-temperature curve (2D curve) and calculated according to the literature (Lazdovica 2016, Lazdovica 2017).

The average value of three experiments is used to compare relative yield of obtained products during pyrolysis without and with catalyst. Probability of confidence interval was equal to $p=0.95$, that complies with Student's distribution coefficient for three experiments – $t_{0.95,3}=4.303$.

3. RESULTS AND DISCUSSION

3.1. Influence of the catalysts on the thermal decomposition of wheat straw

The influence of catalysts on the yield of volatile products and solid residue are shown in Fig. 1. It can be seen that the yield of volatile products and solid residue of wheat straw without catalysts is 74,9% and 25,1%, respectively. It was found that the volatile matter of wheat straw decreased from 74,9% to 47,1%, 46,9% and 72,5%, under the catalyst of CaO, calcined dolomite and CaCO₃, accordingly. This is partially due to the CaO and calcined dolomite can absorb the released carbon dioxide to form CaCO₃ product (Han 2010, Wang 2010).

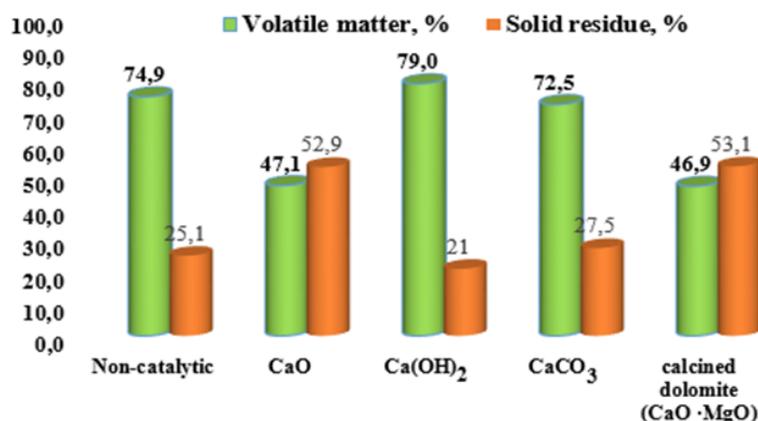


Fig. 1. Influence of calcium – based catalysts on the volatile matter and solid residue of wheat straw

Volatile matter of wheat straw increased from 74,9% to 79,0 by using Ca(OH)₂, which can be explained by the thermal decomposition of catalyst, when heating calcium hydroxide to 500 °C the calcium hydroxide decomposes into calcium oxide and water.

3.2. Influence of the catalysts on the relative yield of non-condensable gases

Composition of the non-condensable gases resulting from the wheat straw treatment with the different calcium-based catalysts is shown in Fig. 2.

It can be clearly seen that the yield of carbon dioxide significantly decreased when the CaO, Ca(OH)₂, and calcined dolomite (CaO·MgO) used as catalysts, compared to the non-catalyzed experiment. Relative yield of carbon dioxide decreased 1.8, 2.5, and 3.0 times when using Ca(OH)₂, CaO, and calcined dolomite (CaO·MgO), respectively, whereas CaCO₃ has not particularly impacted the formation of above mentioned gas. The evolution curve of carbon dioxide without and with calcium

based catalysts proceeded in a wide range of temperature 220 to 550 °C with one peak at T_{max} of 395 °C (non-catalytic), T_{max} of 411 °C (CaCO_3), T_{max} of 385 °C ($\text{Ca}(\text{OH})_2$), T_{max} of 347 °C (CaO), and T_{max} of 379 °C (calcined dolomite). It is known that the CaO is an excellent carbon dioxide sorbent with low costs (Wang 2010, Zhao 2014), the large portion of carbon dioxide from wheat straw pyrolysis is absorbed by CaO , $\text{Ca}(\text{OH})_2$, and CaO in calcined dolomite (see in reactions (I) – (III)).

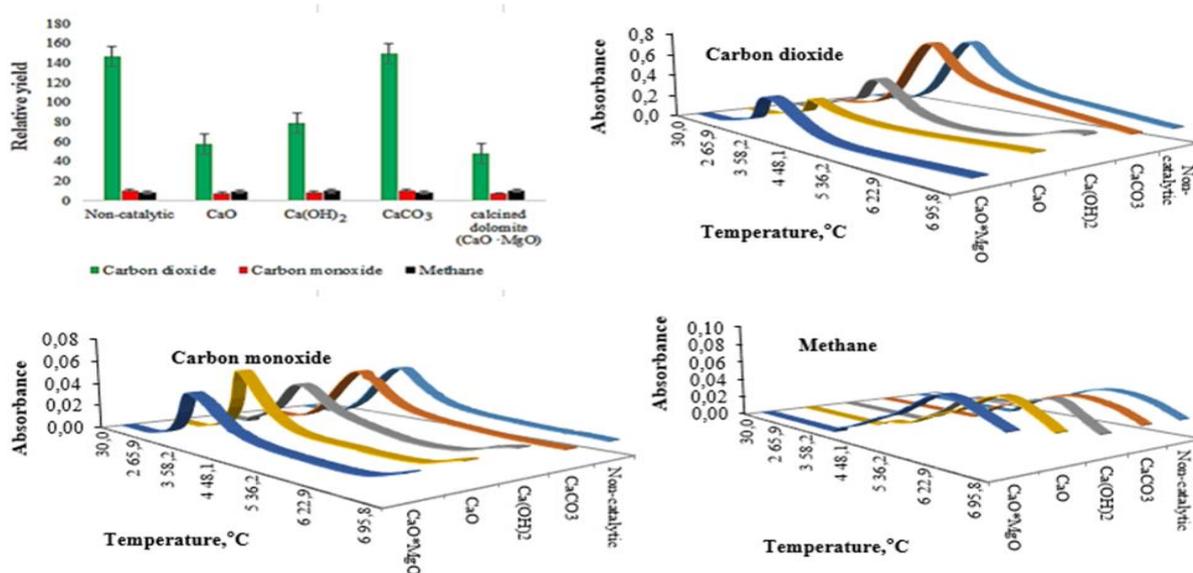
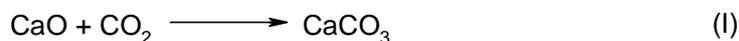
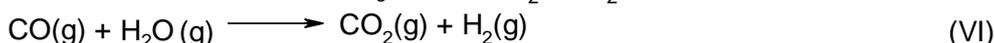
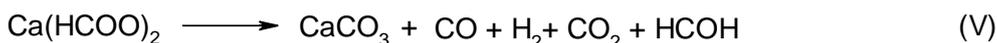
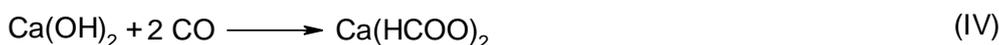


Fig. 2. The evolution of carbon dioxide, carbon monoxide, methane and relative yield of the non-condensable gases during wheat straw pyrolysis without and with catalysts

As shown in Fig. 2, the relative yield of methane increased 1.2, 1.2, and 1.3 times by using $\text{Ca}(\text{OH})_2$, CaO , and calcined dolomite ($\text{CaO} \cdot \text{MgO}$), respectively, whereas CaCO_3 has not impacted the formation of methane. The evolution curve of carbon monoxide without and with calcium based catalysts occurred in the temperature range from 390 to 700 °C with one peak at T_{max} of 612 °C (non-catalytic), T_{max} of 628 °C (CaCO_3), T_{max} of 643 °C ($\text{Ca}(\text{OH})_2$), T_{max} of 643 °C (CaO), and T_{max} of 628 °C (calcined dolomite). The increasing concentration observed for methane, could be related to the promotion cracking reactions since these calcium - based materials have shown some catalytic effect on biomass pyrolysis (Veses 2014, Wang 2010).

As depicted in Fig. 2, the relative yield of carbon monoxide decreased 1.2, 1.4, and 1.5 times by using $\text{Ca}(\text{OH})_2$, CaO , and calcined dolomite ($\text{CaO} \cdot \text{MgO}$), respectively, whereas CaCO_3 has not impacted the formation of above mentioned gas. The evolution curve of carbon monoxide without and with calcium based catalysts occurred in the temperature range from 250 to 600 °C with one peak at T_{max} of 385 °C (non-catalytic), T_{max} of 406 °C (CaCO_3), T_{max} of 369 °C ($\text{Ca}(\text{OH})_2$), T_{max} of 358 °C (CaO), and T_{max} of 363 °C (calcined dolomite). According to the literature, the calcium hydroxide can react with carbon monoxide to produce calcium formate, the thermal degradation products of calcium formate are calcium carbonate, hydrogen, carbon monoxide, formaldehyde, carbon dioxide, and calcium oxide (Liu 2012). It is possible that in case of calcium hydroxide happened above mentioned reactions therefore reduced relative yield of carbon monoxide.

Liu (2012) found that the calcium oxide is a catalyst for the water-gas shift reactions with in situ carbon dioxide sorption because reactions on the calcium oxide surface are limited. By using calcined dolomite, both CaO and MgO can catalyzed the water-gas shift reactions. Similar results for the influence of CaO on the non-condensable gases are reported by other authors for the water-gas shift reactions (Li 2014) and pyrolysis of sawdust (Zhao 2014), wood biomass (Veses 2014), pine sawdust and peanut shell (Zhang 2014). It is possible, that CaO and calcined dolomite catalyzed the water – gas shift reaction on its surface therefore reduced relative yield of carbon monoxide (see in reaction (IV) – (VI)).



3.3. Influence of the catalysts on the relative yield of hydrocarbons

The effect of calcium-based catalysts on the relative yield and evolution curve of hydrocarbons is shown in Fig.3. It can be clearly seen that the CaCO₃ had effect on the production of aromatics whereas the yield of olefins was increased in presence of all calcium-based catalysts, compared to the non-catalytic experiment.

As depicted in Fig.3, the relative yield of aromatics and toluene increased 1.4 times with CaCO₃, other catalysts had negative effect on the formation of aromatics and toluene and gave the smallest amount of aromatic compounds. The relative yield decreased 2.5, 1.9, and 1.5 times, respectively by using CaO, calcined dolomite, and Ca(OH)₂. The evolution curve of aromatics without and with catalysts occurred in the temperature range from 240 to 550 °C with one peak at *T*_{max} of 406°C (non-catalytic), *T*_{max} of 411 °C (CaCO₃), *T*_{max} of 390 °C (Ca(OH)₂), *T*_{max} of 358 °C (CaO), and *T*_{max} of 379 °C (calcined dolomite).

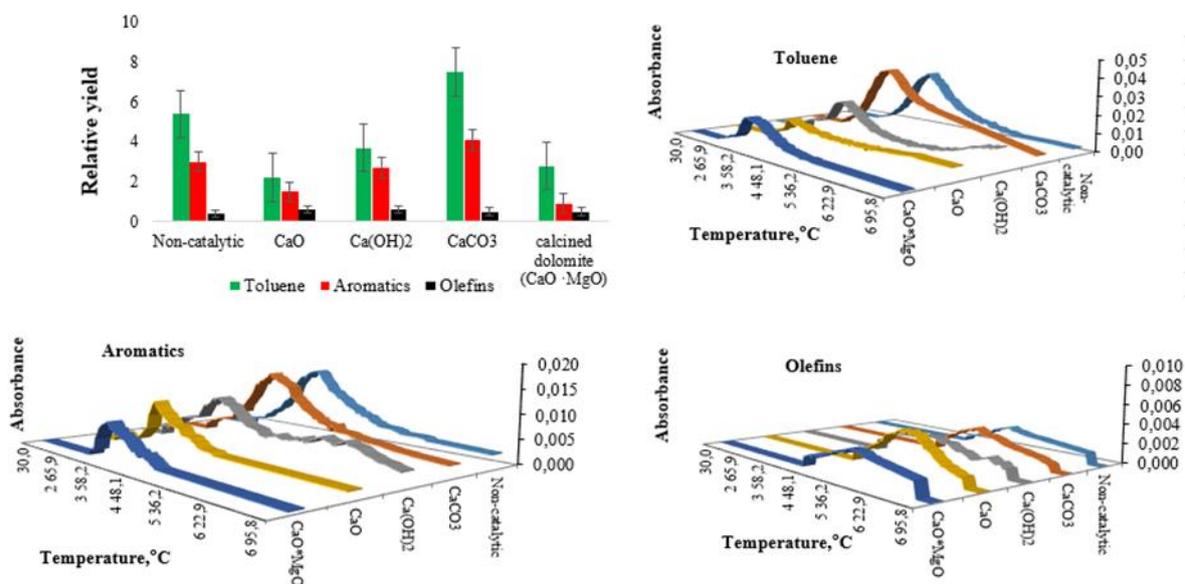


Fig. 3. The evolution of olefins, aromatics, toluene and relative yield of the hydrocarbons during wheat straw pyrolysis without and with catalysts

The evolution curve of toluene without and with catalysts happened in the temperature range from 270 to 570 °C with one peak at T_{max} of 416°C (non-catalytic), T_{max} of 411 °C (CaCO_3), T_{max} of 379 °C ($\text{Ca}(\text{OH})_2$), T_{max} of 369 °C (CaO), and T_{max} of 379 °C (calcined dolomite). Mostly, the source of the formation of aromatic compounds from pyrolysis of wheat straw is lignin. Aromatic hydrocarbons are formed upon demethoxylation and dehydration reactions from guaiacol-type, syringol-type and phenol-type compounds (Shen 2015). It is possible that the formations of aromatic compounds are affected due to the thermal degradation of lignin. According to the literature, the calcium - based catalysts such as CaO , calcined dolomite (Veses 2014, Zhao 2014), as well as MgCl_2 (Hwang 2015) slightly favour the formation of heavy polycyclic aromatic hydrocarbons thereby decreased in the amount of lignin monomer. It is possible that the CaCO_3 promoted dehydroxylation reaction of methylphenol thereby affecting formation of toluene. Similar results for the influence of calcium-based catalysts on the aromatic compounds are reported by other authors for the pyrolysis of sawdust (Zhao 2014), wood biomass (Veses 2014), wheat straw (Han 2010). The CaO , $\text{Ca}(\text{OH})_2$, calcined dolomite showed low selectivity to aromatics compared to the CaCO_3 and non-catalytic process, the rank order of aromatics selectivity was $\text{CaCO}_3 > \text{Ca}(\text{OH})_2 > \text{calcined dolomite} > \text{CaO}$.

As shown in Fig. 3, the CaO and $\text{Ca}(\text{OH})_2$ were the most active in the formation of olefins in comparison to other catalysts. The relative yield of olefins increased 1.5 times with CaO and $\text{Ca}(\text{OH})_2$, and 1.3 times with CaCO_3 and calcined dolomite. The evolution profile of olefins without and with catalysts occurred in the temperature range from 440 to 700 °C with one peak at T_{max} of 536°C (non-catalytic), T_{max} of 556 °C (CaCO_3), T_{max} of 530 °C ($\text{Ca}(\text{OH})_2$), T_{max} of 592 °C (CaO), and T_{max} of 582 °C (calcined dolomite). The formation of olefins is connected with dehydration of alcohols, the dehydration reaction can be catalyzed by various types of Brønsted and Lewis acids and bases such as MgO and CaO ; as shown in Fig. 4, the relative yield of compounds containing hydroxyl group (alcohols, LG, Xylosan) decreased by using all catalysts. The CaO and $\text{Ca}(\text{OH})_2$ showed selectivity of olefins compared to CaCO_3 , calcined dolomite, and non-catalytic process, the ranking order of olefins selectivity was $\text{CaO} \approx \text{Ca}(\text{OH})_2 > \text{CaCO}_3 \approx \text{calcined dolomite}$.

The CaCO_3 catalyst provided the highest aromatics selectivity, whereas CaO catalyst showed highest olefins selectivity.

3.4. Influence of the catalysts on the relative yield of compounds containing carbonyl, carboxyl, and hydroxyl groups

Composition of the compounds containing carbonyl and carboxyl groups resulting from the wheat straw treatment with the different calcium-based catalysts is shown in Fig. 4.

It can be clearly seen that the yield of organic acids significantly decreased when the CaO , $\text{Ca}(\text{OH})_2$, and calcined dolomite ($\text{CaO} \cdot \text{MgO}$) used as catalysts, compared to the non-catalyzed experiment. Relative yield of organic acids decreased 2.5, 2.4, 2.2, and 1.1 times when using calcined dolomite ($\text{CaO} \cdot \text{MgO}$), CaO , $\text{Ca}(\text{OH})_2$, and CaCO_3 .

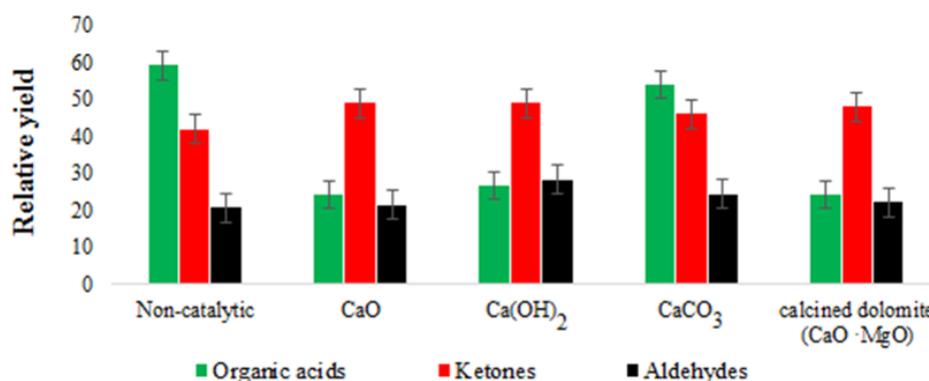
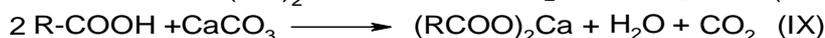
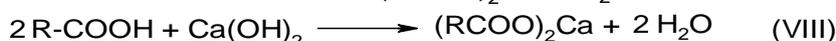


Fig. 4. The relative yield of the compounds containing carbonyl and carboxyl groups during wheat straw pyrolysis without and with catalysts

Acetic and formic acids are predominant carboxylic acids in the bio-oils from lignocellulosic biomass. It is known that acid compounds can react with calcium - based catalysts to produce the calcium carboxylate salt ((see in reaction (VII) – (IX)).



The thermal decomposition products of calcium carboxylate salt are calcium carbonate, formaldehyde, acetone, and acetaldehyde (see in reaction (X) – (XII)) (Han 2010, Hlavsova 2014, Veses 2014, Wang 2010); as shown in Fig.4, the relative yield of aldehydes and ketones increased by using all the catalysts.



As shown in Fig. 5, all catalysts decreased the formation of alcohols, LG and xylosan. The relative yield of alcohols and anhydrosugars decreased 2.2 times with CaO and Ca(OH)₂, 1.9 times with calcined dolomite, 1.1 times with CaCO₃. These results are consistent with Patwardhan (2010) who found that with different calcium salts (CaCl₂, Ca(OH)₂, Ca(NO₃)₂, CaCO₃, and CaHPO₄) the levoglucosan yield decreased, and formic acid and acetol yield increased. Obtained results confirmed that all used calcium - based catalysts catalysed deoxygenation in the form of dehydration.

As shown in Fig.5, the relative yield of water increased by using all the catalysts. The relative yield of water increased 3 times with Ca(OH)₂, 2 times with CaO, 1,8 times with calcined dolomite, and 1.1 times with CaCO₃. It can be clearly seen that Ca(OH)₂ had substantial effect on production of water, which can be explained by the thermal decomposition of catalyst, when heating calcium hydroxide to 500 °C the calcium hydroxide decomposes into calcium oxide and water.

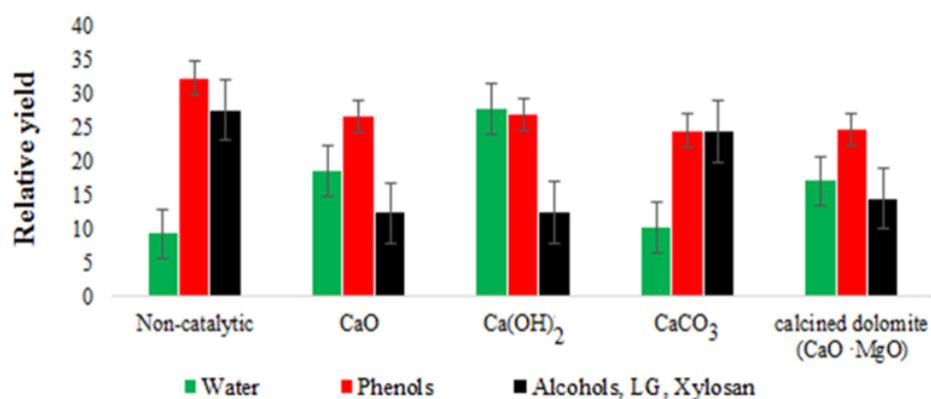


Fig. 5. The relative yield of the compounds containing hydroxyl group during wheat straw pyrolysis without and with catalysts

As depicted in Fig. 5, all calcium – based catalysts decreased the formation of phenols. The relative yield of phenols decreased 1.3 times with calcined dolomite and CaCO_3 , 1.2 times with CaO and Ca(OH)_2 . According to the literature, CaO and calcined dolomite reduced the formation of phenolic compounds and promoted formation of polyaromatics (Veses 2014, Zhao 2014).

The presence of all calcium – based catalysts catalyzed deoxygenation of volatile compounds from wheat straw pyrolysis by dehydration reaction and all catalyst can be converted organic acids through neutralization (calcium salt), thermal and catalytic cracking.

4. CONCLUSION

All catalysts, except Ca(OH)_2 , decreased the volatile matter and increased the solid residue of wheat straw. All catalysts promoted formation of olefins whereas CaCO_3 advanced formation of aromatics. The presence of all calcium – based catalysts catalysed deoxygenation of volatile compounds from wheat straw pyrolysis by dehydration reaction and all catalyst can be converted organic acids through neutralization (calcium salt), thermal and catalytic cracking.

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