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Full Length Research Paper

Influence of metal elements on the evolution of CO and CH_4 during the pyrolysis of sawdust

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Metal elements in biomass ash have been considered to affect the decomposition of large molecule during the pyrolysis of biomass. In this paper, effect of metal elements on the evolution of carbon monoxide (CO) and methane (CH_4) was investigated during the pyrolysis of sawdust in a fixed bed reactor and species were detected by Fourier Transform Infrared analyzer. Results showed that all the metal additions restrained the yields of CO and CH_4 and the quantity order of production was Fe_2O_3<ZnO<NaCl<CaO<KCl< Al_2O_3<No-addition. The addition of Al_2O_3, Fe_2O_3 and ZnO shortened the completion time of CO and CH_4. Statistical analysis demonstrated that all the metal additions lowered the reaction rate of biomass pyrolysis dynamically.

Key words: Biomass, pyrolysis, carbon monoxide, methane, metal element.

INTRODUCTION

Researches on biomass-utilization have become a hot spot in recent years, because biomass is considered as a fuel with no emission of carbon (IV) oxide (CO_2). This tends to reduce the problem of greenhouse effect especially as the content of nitrogen and sulphur in biomass is low. The utilization of biomass mainly focuses on the transformation of thermochemistry (Baratieri et al., 2008; Ross et al., 2008; Zabaniotou et al., 2008; Zheng et al., 2008) and the process of pyrolysis is an important step during the process. The ash content in biomass is lower than coal, however, biomass contains much higher alkali element, which has been considered to affect the decomposition of large molecule during the pyrolysis of biomass (Jensen et al., 1998). Therefore, it is necessary to demonstrate how metal elements affect the pyrolysis of biomass and studies have been carried out on this. However, due to the differences in experimental conditions, conclusions are still not uniform. Results of Pengmei et al. (2004) and Desmond et al. (1991) showed that nickel-based catalysts and dolomite can reduce the production of carbon monoxide (CO) and methane (CH_4) during the pyrolysis of biomass; but other results considered nickel to promote the generation of CO and CH_4, with little effect from calcium and potassium (Yang et al., 2006). Experiments under different heating rate showed that the effect of sodium and aluminum on the evolution of gas species during pyrolysis of biomass is different depending on the different heating velocity (Ilknur and Sevgi, 2008).

Consequently, in this study, the influence of metal elements (aluminum (Al), calcium (Ca), iron (Fe), potassium (K), sodium (Na) and zinc (Zn)) on the fast-pyrolysis of sawdust in a fixed bed was investigated and Fourier Transform Infrared (FTIR) analyzer was used to detect the production of CO and CH_4. Statistical analysis was performed to demonstrate the effect of metal element addition on the pyrolysis of sawdust kinetically.

MATERIALS AND METHODS

Materials

The sawdust used in the experiment was from a wood factory around Xi'an in Shaanxi Province, china and the elemental analysis and proximate analysis of sawdust is shown in Table 1. The addition of metal elements (Al, Ca, Fe, K, Na and Zn) corresponds to metallic compounds (Aluminium oxide (Al_2O_3), Calcium Oxide (CaO), Iron(III) oxide (Fe_2O_3), potassium chloride (KCl), sodium chloride (NaCl) and zinc oxide (ZnO)) with analysis purity. The diameters of sawdust and its addition were less than 148 μm. 20 mg sawdust was put in a reactor with 100 mg metal additions during the experi-

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Table 1. Proximate analysis, elemental analysis and calorific value of coal.

Proximate analysis (%, w/w)			Elemental analysis (%, w/w)				
M_{ar}	A_{ar}	V_{daf}	C_{ar}	H_{ar}	N_{ar}	O_{ar}	S_{ar}
9.87	0.42	76.77	44.75	4.98	0.12	39.85	0.01

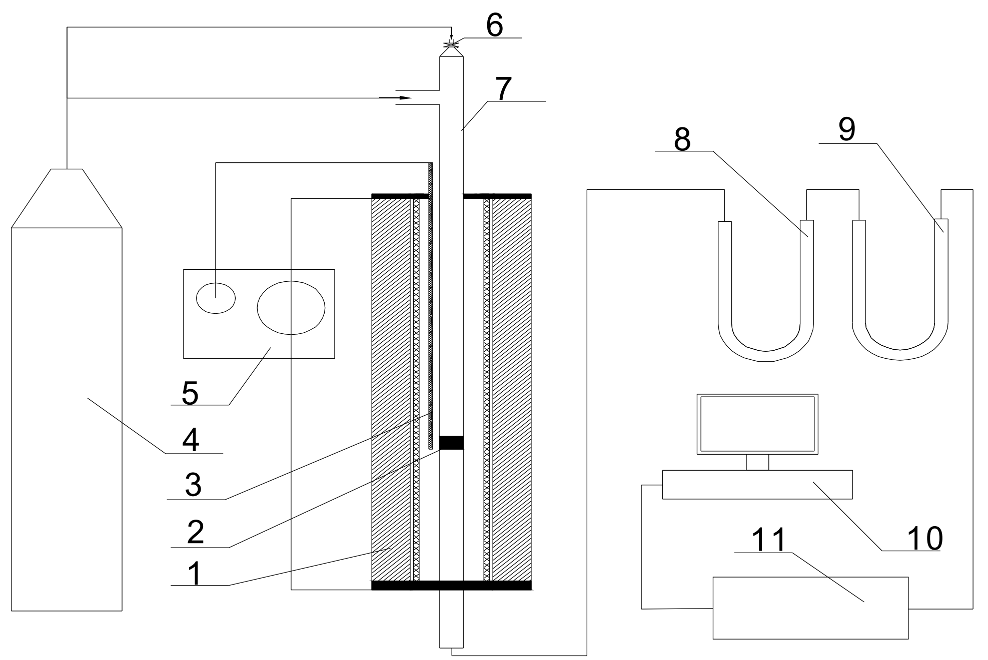


Figure 1. Schematic diagram of the experimental system. 1= Tube furnace; 2 = Orifice; 3 = Thermacouple; 4 = Nitrogen; 5 = Temperature controller; 6 = Feeder of biomass and metal-addition; 7 = Quartz reactor; 8 = Filter-1; 9 = Filter-2; 10 = Data acquisition computer; 11 = FTIR analyzer.

mental process.

Experimentation

The experimental system is shown in Figure 1. High-purity (99.999 %) nitrogen was divided into two groups, one of which was side-blown into the reactor directly to keep the reducing atmosphere while the other was added above the reactor by blowing the sawdust and metal addition into the reactor. The sawdust and metal addition mixed well and lands on the orifice to react further. The products of biomass pyrolysis from the reactor, flow through two-stage filters to remove the solids and tar in the flue gas and are then detected online in FTIR analyzer. After the reaction, oxygen was blown into the reactor to clear the solid residues and repeated experiments were carried out to keep the experimental repeatability less than 5%. Literatures showed that pyrolysis of biomass was completed at a temperature of 673K, which was selected as the constant reaction temperature during the fast pyrolysis of biomass and the flow rate of nitrogen was constant (200 $ml.min^{-1}$).

The experiment was carried out in a quartz reactor, which was 18 mm in inner diameter and 1000 mm in length. An electric furnace with a siliconcarbide (SiC) tube as electrothermal element supplied heat to the reactor and could work continuously at a temperature as high as 1473K and the constant temperature heating zone was longer than 600 mm. A Pt-Rh/Pt thermocouple was used to measure the reaction zone temperature controlled by a SHIMADEN FP93 PID regulator. The precision of the temperature control was ±2K.

The concentration of CO and CH_4 in flue gas was detected on-line by a Helsinki made DX-4000 FT-IR gas analyzer, which has a 1.07 L gas analysis cell with a path of 5 m, resolution of 8 cm^{-1}, response time <120 s, wave-number range of 900 - 4200^{-1} and scan frequency of 10 spectra/s. The lowest detectable concentration was 1 ppm and the estimated uncertainty limits of measurements were estimated to be within ±2%.

RESULTS AND DISCUSSION

The infrared spectroscopy of flue gas from biomass pyrolysis is shown in Figure 2. The spectroscopy corresponded to the time when the concentration of CO and CH_4 reaches the highest during the reaction process of sawdust. The test condition of sodium-addition (Figure 2a) was selected and compared with the condition with no addition (Figure 2b). From the figures, it could be deduced that when metal compound was added, the characteristic peaks (2000 and 2200 cm^{-1}) of CO_2 and CO were weakened greatly even as the characteristic

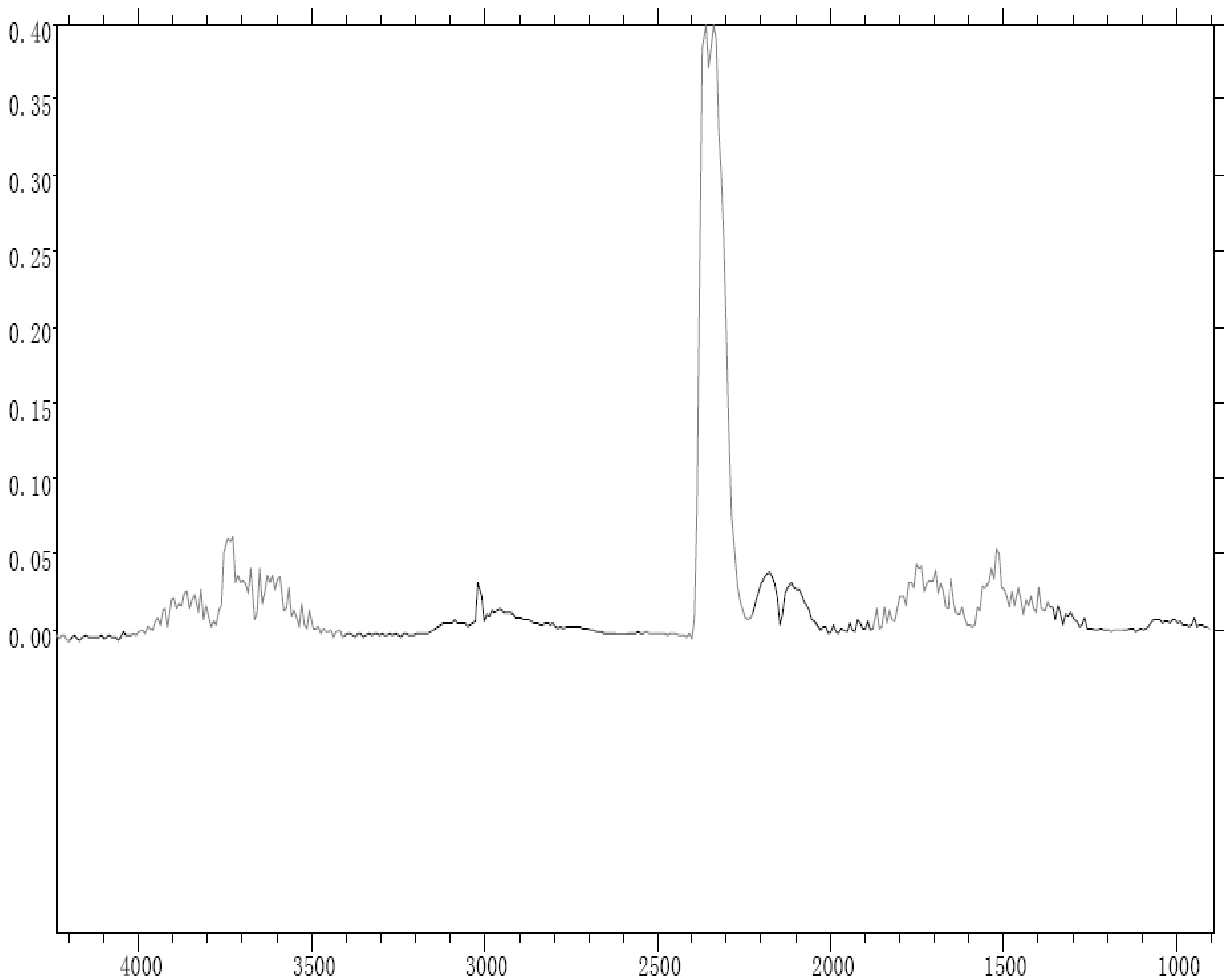


Figure 2a. Comparison of the infrared spectroscopy with Sodium-addition.

peaks (1250 and 3000 cm^{-1}) of CH_4 was also weakened. It demonstrated that the addition of metal compounds has restrained the pyrolysis of sawdust.

In order to quantitatively compare the yields of CO and CH_4 during the different test conditions, a relative yield was defined as:

$$q = \frac{Q_\tau}{Q_{total}}$$

Where, τ = the reaction time from the addition of materials; Q_τ = the total mass of CO or CH_4 until the time τ, and Q_{total} = the total mass when the pyrolysis was completed.

Q_τ is calculated as follows:

$$Q_\tau = \int_0^\tau C \times V \times M \times d\tau$$

Where, C = the concentration of CO or CH_4; V = the constant flow rate 200 $ml.min^{-1}$, and M = the molecular weight.

In this research, τ_i is defined as the original time when CO or CH_4 begins to be generated and τ_f as the completion time when the relative yield has reached 0.9.

Effect of metal addition on CO

Figure 3 illustrates the change of CO concentration during the process of sawdust pyrolysis with or without metal addition and the relative yields of different test conditions were also compared.

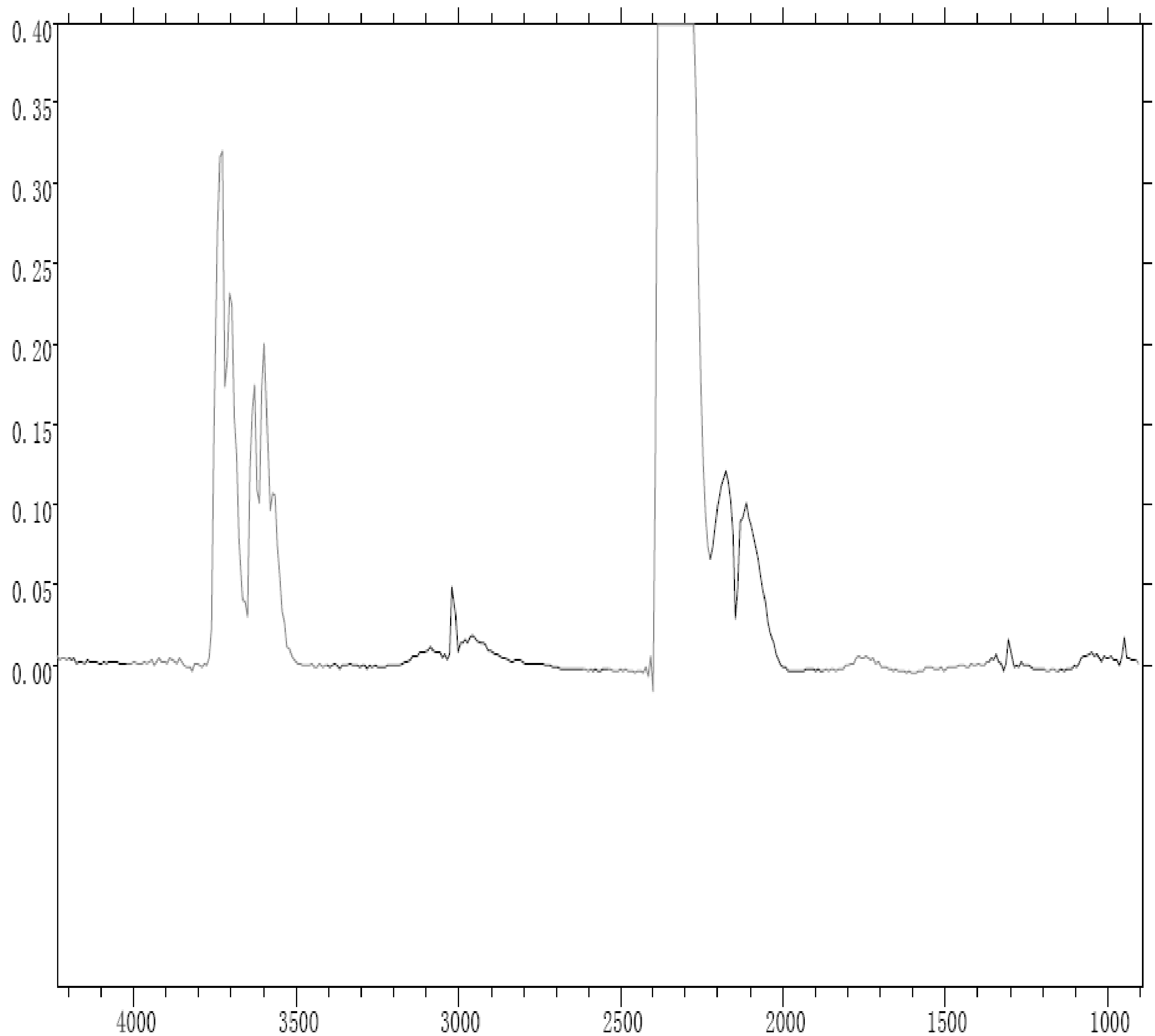


Figure 2b. Comparison of the infrared spectroscopy with no-addition.

It was shown that τ_i for CO was shortened when Al_2O_3/Fe_2O_3/ZnO was added and τ_i changes little when CaO/KCl/NaCl were added. However, the complete time τ_f, could only be significantly shortened with the addition of Fe_2O_3 and with little effect from the addition of other metal. By comparing the peaks of CO concentration with and without metal addition, it could be seen that all the metal addition weakened the intensity of peaks except for Al_2O_3.

Figure 4 demonstrates the effect of metal addition on Q_{total} of CO, which showed that the effect of Fe_2O_3 was the largest and that of Al_2O_3, the smallest.

Effect of metal addition on CH_4

Figure 5 has shown the effects of metal addition on the evolution of CH_4. To agree with the effects on CO, τ_i for CH_4 was also shortened by the addition of Al_2O_3/Fe_2O_3/ZnO while the others had little effect. Compared with the effect on the peaks of CO in Figure 3, the effect of metal addition on the peaks intensity of CH_4 was larger. The addition of Al_2O_3/KCl/NaCl weakened the peaks intensity of CH_4 by 50%. The effect of metal addition on Q_{total} of CH_4 is shown in Figure 6. It could be seen that, with CO, the order of quantity was $Fe_2O_3 < ZnO < NaCl < CaO < KCl <$

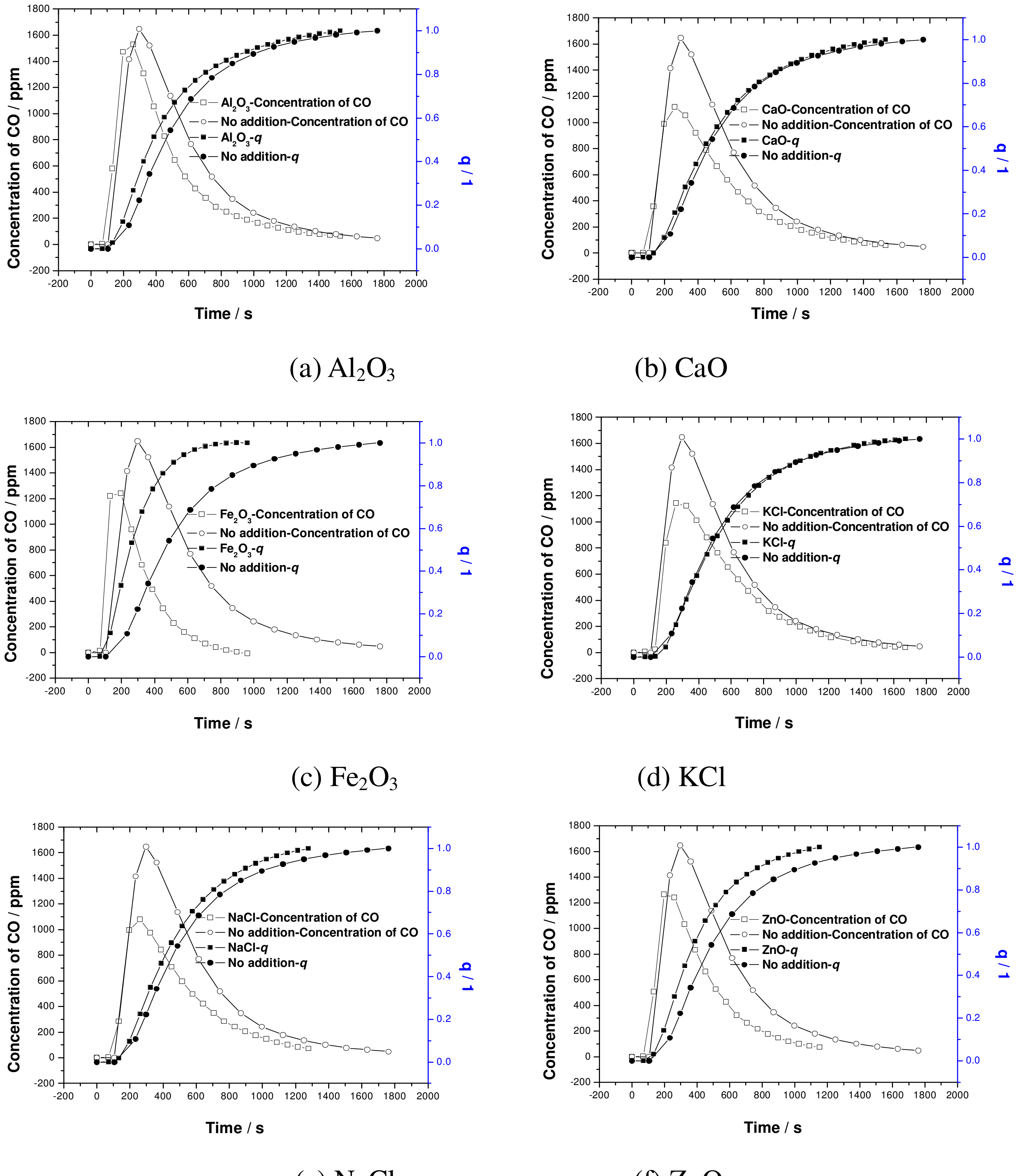


Figure 3. Effect of metal addition on the evolution of CO.

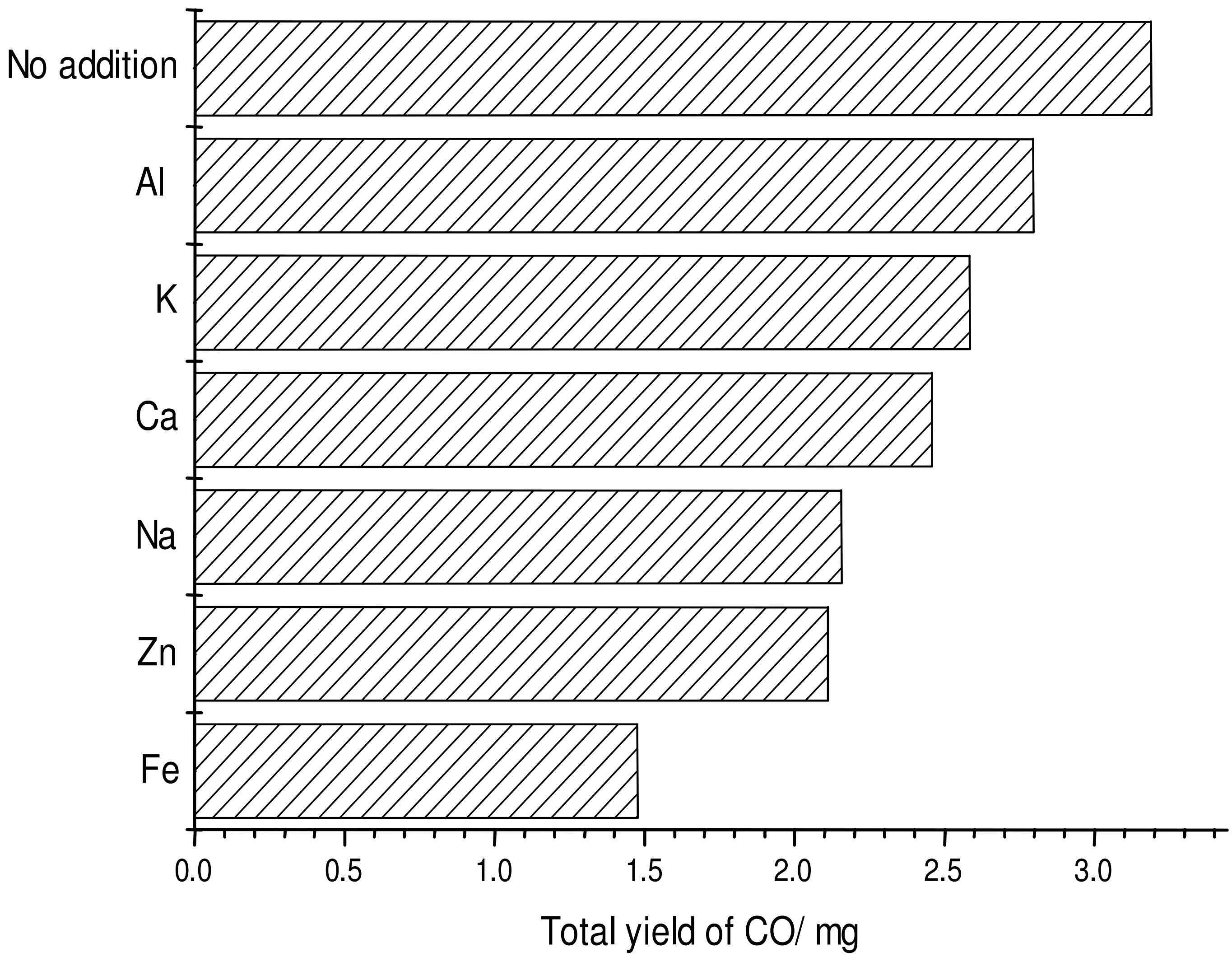


Figure 4. Effect of metal addition on the total yield of CO.

Al_2O_3<No-addition.

Effect of metal addition on reaction rate

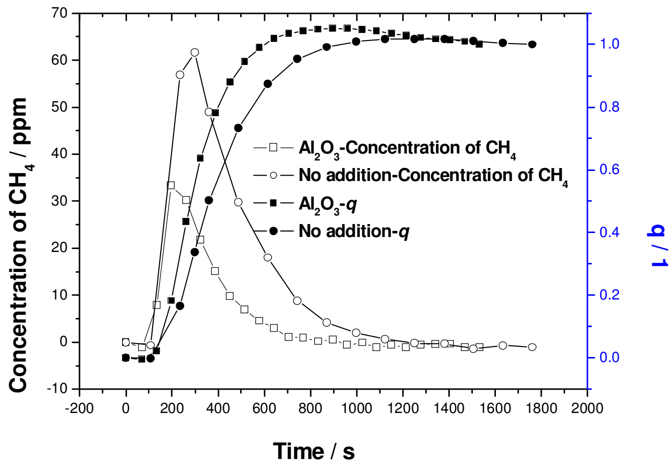
The results showed that the yield of CO is much higher than that of CH_4. Therefore, to dynamically illustrate the effect of metal addition on the pyrolysis of sawdust, the average reaction rate ω was defined on the basis of Q_f and τ_f.

$$\omega = \frac{Q_f}{\tau_f}$$

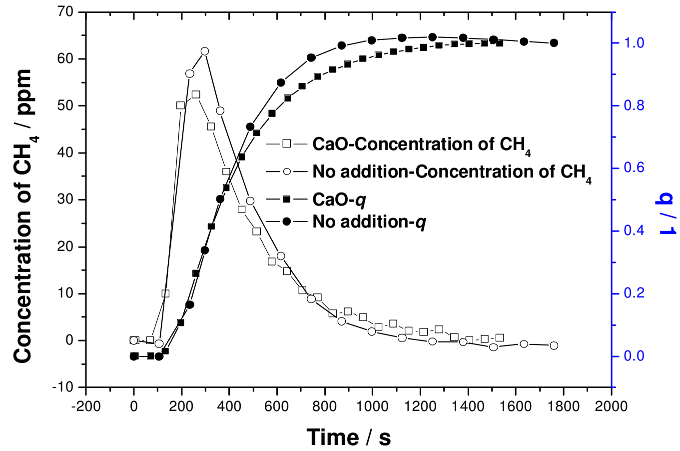
Figure 7 gives the comparison of reaction rate for different metal addition. It showed that the additions lowered the reaction rate. The order of reaction rate was No-addition>Al_2O_3>Fe_2O_3>ZnO>KCl >CaO>NaCl.

Conclusion

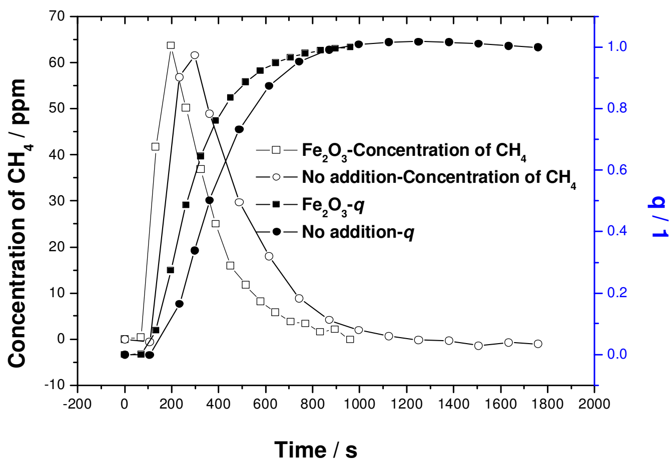
In this paper, the influence of metal elements on the fast-pyrolysis of sawdust was investigated and FTIR analyzer was used to detect the yields of CO and CH_4. Statistical analysis was performed to demonstrate the effect of metal element addition on the pyrolysis of sawdust kinetically. The conclusions are summarized as follows: (1) All the metal additions inhibited the yields of CO and CH_4 and the order of inhibiting ability was Fe_2O_3>ZnO> NaCl> CaO >KCl>Al_2O_3; (2) The addition of Al_2O_3/Fe_2O_3/ZnO shortens the completion time of CO and CH_4, especially for Fe_2O_3 while the others have relatively little effect; (3) All the metal additions lowered the reaction rate of biomass pyrolysis and the reaction rate order was no-addition>Al_2O_3>Fe_2O_3> ZnO>KCl >CaO>NaCl.



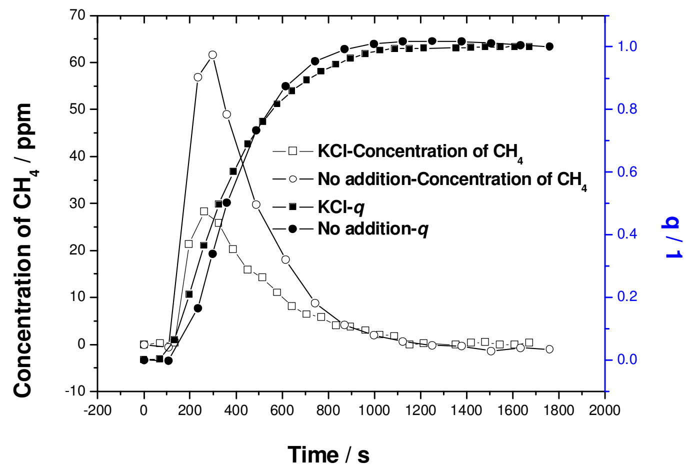
(a) Al_2O_3



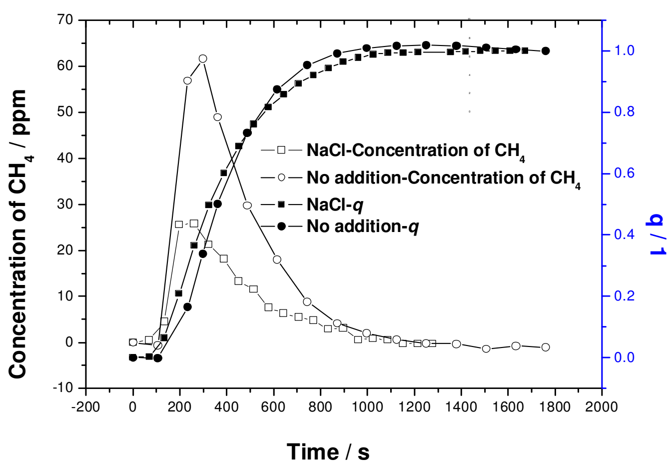
(b) CaO



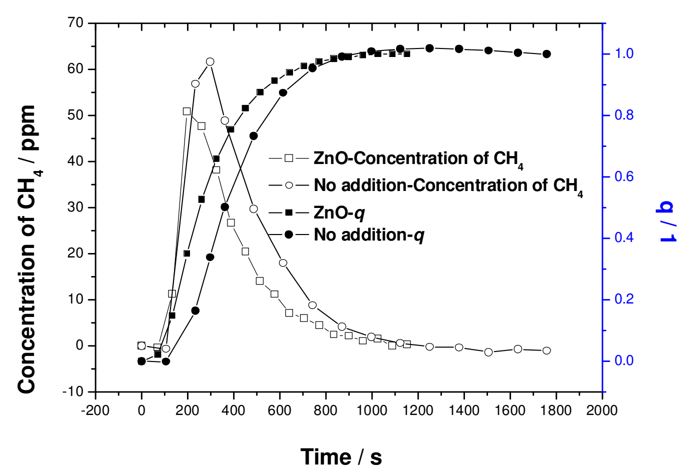
(c) Fe_2O_3



(d) KCl



(e) NaCl



(f) ZnO

Figure 5. Effect of metal addition on the evolution of CH_4.

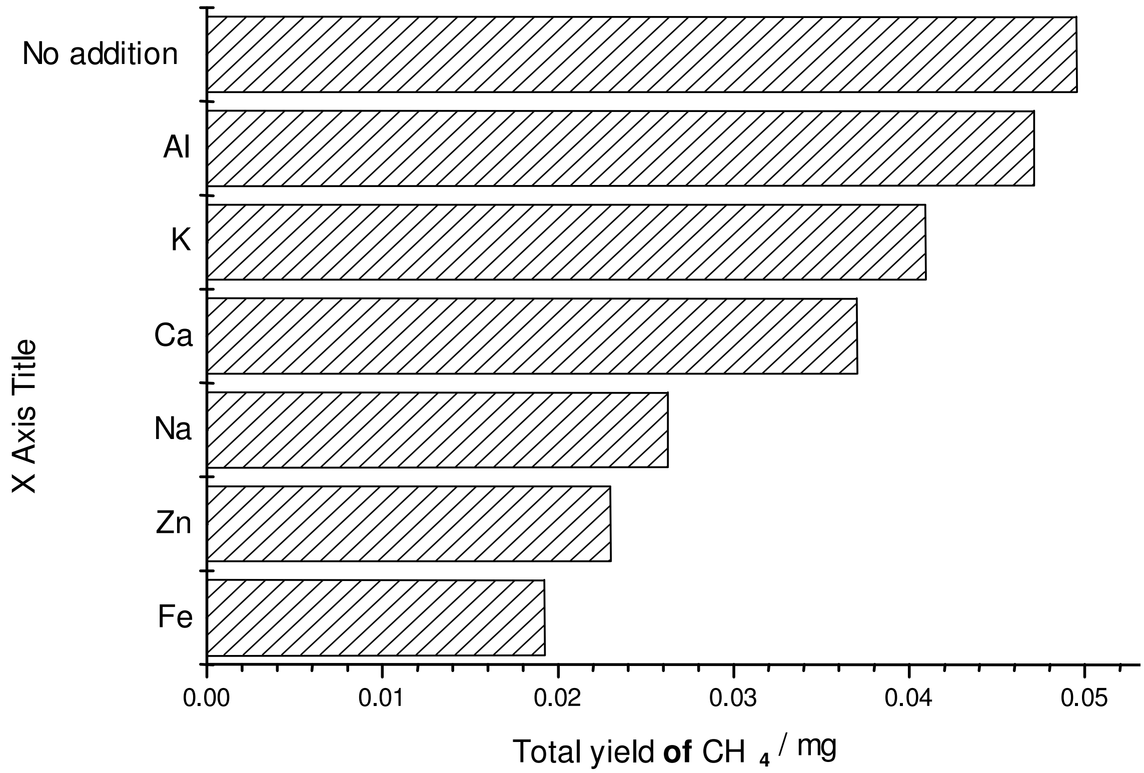


Figure 6. Effect of metal addition on the total yield of CH_4.

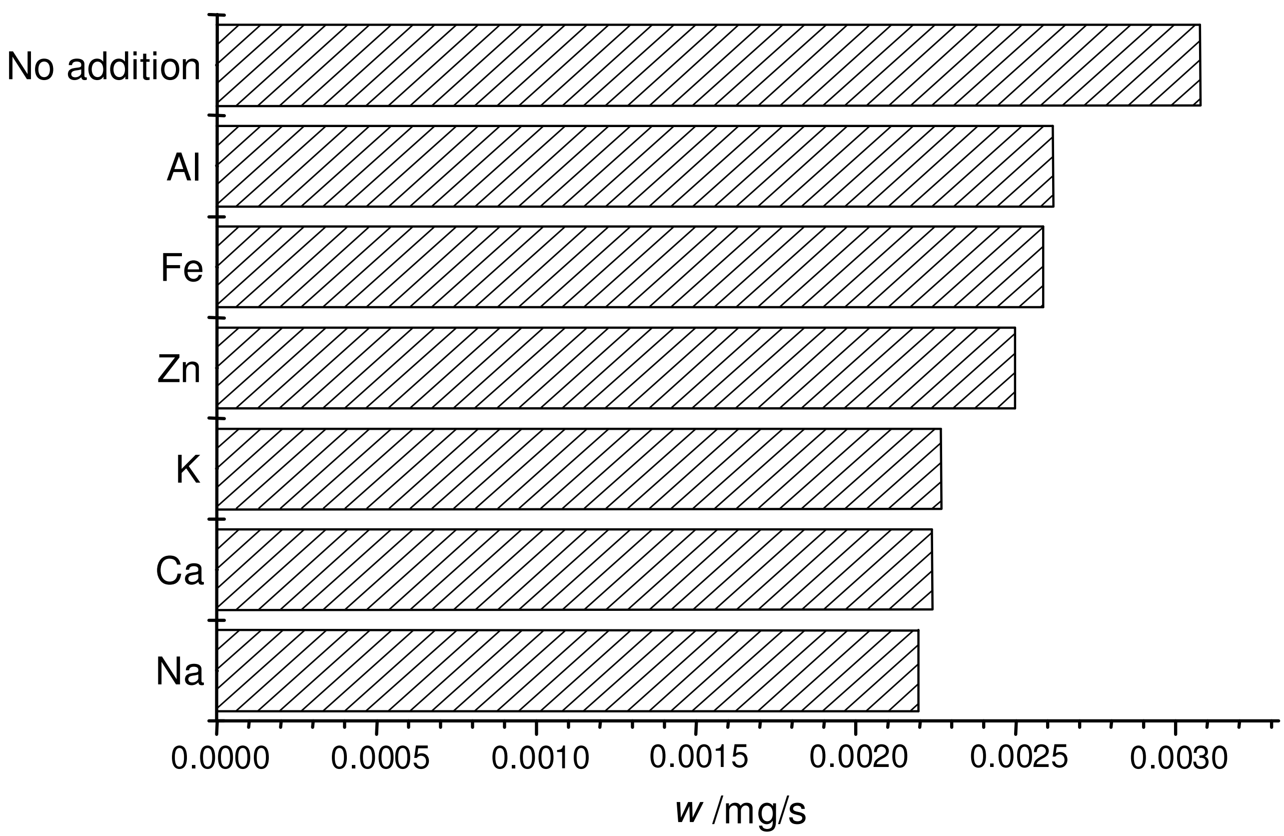


Figure 7. Effect of metal addition on the reaction rate of sawdust pyrolysis.

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