CHAPTER VII

TEMPERATURE-PROGRAMMED COMBUSTION OF SEWAGE SLUDGE CHARS PREPARED BY THERMAL DECOMPOSITION UNDER N_2 AND CO_2 ATMOSPHERE

7.1 Abstract

Temperature-programmed combustion of sewage sludge chars which were prepared under different pyrolysis atmospheres, N_2 and CO_2, within the temperature range of 350-750°C were studied. The results showed that the reactivities of all char samples become less reactive with the increase of pyrolysis temperature as indicating by the decrease of the maximum reactivity (R_{max}) and the increase of the temperature at the maximum (T_m). R_{max} and T_m correlate well with the total pore volume. This might be due to the increase of the total pore volume of chars as a function of pyrolysis temperature. However, both R_{max} and T_m cannot be correlated with BET surface area of chars. Utilizing of CO_2 during the pyrolysis experiment were found to be insignificant on the combustion reactivity of prepared chars but BET surface area and total pore volume of chars prepared were found to increase especially at high pyrolysis temperature.

7.2. Introduction

Due to the technological and economical problems, the direct combustion of alternative fuels (biomass, wastes and low quality coals) is limited at this present time. There are many difficulties such as the heterogeneity nature depending on the sources, the material characteristics (heating value, moisture content and ash content) including the behavior during processes (ignition characteristics, agglomeration, fouling, and corrosion phenomena in the combustor) of such materials. However, the use of these materials has been considered as important advantages. Not only biomass represents as renewable resources but also considers as CO_2 neutral fuels. For wastes, they can be taken advantage of their energy content instead of fate to landfill [1].

Although the combustion of coals has been studied and commercialized, the differences in the combustion profile is expected. Unlike coals, biomass and waste

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materials comprise of complex constituents and vary in their amount. Focusing on the sewage sludge, the sewage sludge combustion technology was studied [2]. In combustion processes, two important stages are always present in the solid phase [1, 3]. The first stage is the pyrolysis stage (essentially promoted by thermal mechanisms) followed by a char combustion stage. Pyrolysis and combustion stage may be sequential or contemporary, depending on the feature of the process considered [3]. Therefore, the individual study of pyrolysis process has been studied in many literatures [4-7] but there is limited information about sewage sludge char combustion.

According to the previous work [8], sewage sludge was thermal decomposed under inert (N_2) and mild oxidative (CO_2) atmospheres. By pyrolyzing under CO_2 atmosphere, the textural and chemical surface properties of char were somewhat altered compare to that of under N_2 atmosphere [9]. This might affect to the reactivity for the subsequence combustion. Therefore, in this contribution, the investigation was to study the reactivity for the subsequent combustion of the sewage sludge chars. The influences of the different pyrolysis conditions on the combustion reactivity of chars toward air were examined.

7.3 Experimental

Sewage sludge from an urban wastewater treatment plant was used as a starting material in the pyrolysis experiments. The sludge contains mainly of volatile matter and ash content of 43 and 46%, respectively, a small amount of moisture and fixed carbon with 6 and 5%, respectively, can be found in this type sludge. Other selected physical and chemical characteristics along with the heavy metal content for this sewage sludge are given in Table 7.1 and 7.2.

The pyrolysis of the sewage sludge was carried out in a horizontal stainless-steel tubular reactor which is placed in an electrical furnace. The flow of a 100 ml min^{-1} of N_2 and CO_2 was provided for an N_2 and CO_2 atmospheres, respectively. Different pyrolysis temperatures (350-750°C) were studied. The sample are referred to N350, N450, N550, N650 and N750 where N represents char sample prepared under N_2 atmosphere and the number represent the pyrolysis temperature in Celsius. In cases of CO_2 atmosphere, N is altered to C, indicating the sample prepared under the CO_2 atmosphere.

For subsequence combustion, non-isothermal reactivity (up to 800°C) toward air (20 ml min^{-1}) of sewage sludge chars (~10 mg), particle size of 20/50 mesh, were investigated in a TG7 Perkin-Elmer thermogravimetric analyzer. The heating rate was 20°C min^{-1} in all cases. Three repeated experiments were accomplished for data confirmation. The thermogravimetric (TG) and differential themogravimetric (DTG) data were used to differentiate the reactivity behavior as well as to provide the following parameters. From DTG curves; T_v, temperature at the beginning of the reaction (°C); T_m, temperature at the maximum (°C); T_e, temperature at the end of the reaction (°C); t_b, burn-out time (s); and R_{max}, maximum reactivity at T_m (wt.% s^{-1})

Textural properties such as BET surface area, micropore surface area, and total pore volume of the sewage sludge chars were determined by the physical adsorption of N_2 at 77 K using a QUANTACHROME AutoSorb-1 analyzer. The BET surface area was calculated. The micropore surface area and total pore volume were calculated by the t-method.

Table 7.1 Proximate analysis, char yields, and textural properties of raw sewage sludge and chars obtained from pyrolysis

	Raw	N350	N450	N550	N650	N750	C350	C450	C550	C650	C750
Proximate analysis[a]											
Volatile (wt.%)	41.0	18.7	13.4	10.6	8.6	6.5	18.8	13.6	10.7	7.3	5.7
Ash content (wt.%)	43.5	65.6	68.9	71.9	73.9	76.6	65.6	69.1	71.6	77.0	78.9
Fixed carbon (wt.%)	15.5	15.7	17.7	17.5	17.5	16.9	15.6	17.3	17.7	15.7	15.4
Char yield (wt.%)[b]	-	76.5	67.5	59.6	60.5	54.9	74.3	65.5	58.5	57.3	52.4
Textural properties											
BET surface area ($m^2 g^{-1}$)	3	14	15	15	16	34	16	18	20	37	61
Micropore ($m^2 g^{-1}$)[c]	-	-	-	-	-	4	-	-	-	4	20
Total pore volume ($mm^3 g^{-1}$)[c]	12	41	48	57	69	78	52	59	68	78	89

[a] free moisture basis

[b] char yield after pyrolysis of raw sewage sludge at a given temperature

[c] obtained by applying *t*-plot method

Table 7.2 Metal content of dried sewage sludge (mg kg^{-1})

Metal	As	Cd	Cu	Hg	Mo	Ni	Pb	Se	Zn
Raw sludge	0.2	1.7	573.3	1.8	6.3	316.0	21.1	5.6	1639.5

7.4 Results and discussion

7.4.1 Proximate analysis and textural properties

Proximate analysis of the raw sludge and their char obtained from pyrolysis under either N_2 or CO_2 atmospheres were shown in Table 7.1. The results showed that proximate composition of char samples was varied depending on the pyrolysis temperature at which the chars were prepared regardless of the atmospheric gas used. The volatile matter was found in the range of 5.7-18.8 wt.% and ash content was varied between ca. 65.6-78.9 wt.%. The volatile matter was found to decrease whilst the ash content was found to increase as a function of the pyrolysis temperature. For example, the volatile matter of C750 decreased from 18.8 to 5.7 wt.% whilst the ash content of C750 increased from 65.6 to 78.9 wt.% as a function of pyrolysis temperature.

For char yields, in Table 7.1, the results showed that char yields were varied depending on the pyrolysis temperature at which the chars were prepared. They were in the range of 52.4-76.5 wt.% and decrease as a function of pyrolysis temperature. They were 76.5 wt.% after pyrolyzed at 350°C and 54.9 wt.% after pyrolyzed at 750°C. However, char yields were found to slightly decrease when CO_2 atmosphere was introduced. Similar finding was reported elsewhere [10, 11].

BET surface area and total pore volume were increased as a function of pyrolysis temperature and they were in the range of 14.0-61.0 m^2 g^{-1} and 41.0-89.0 mm^3 g^{-1}, respectively [12] which were comparable to that of reported elsewhere [13]. Moreover, for char prepared at 750°C, BET surface area of chars was increased up to 61.0 m^2 g^{-1} while and total pore volume of chars was increased up to 89.0 mm^3 g^{-1} by introducing CO_2. Moreover, micropore surface area was only found for the char prepared at 750°C and under CO_2 atmosphere. From these results, the increase in BET surface area, total pore volume and the micropore surface area might be due to CO_2

disclose the less accessible pore of char due to a favorable reaction rate of CO_2 gasification at this temperature [14].

7.4.2 Temperature-programmed combustion of sewage sludge chars

The TG and DTG profiles in air of the chars prepared under N_2 and CO_2 atmospheres at 350, 550 and 750°C were shown in Figure 7.1(a), 7.1(b) and 7.1(c), respectively. The results showed that DTG profiles show 3 typical peaks. The first peak took place at the beginning of DTG profile in the temperature range of 105-120°C attributing to the loss of adsorbed water, corresponding to the slightly decrease in the TG profiles. The second peak took place in the temperature range of 450-555°C. This peak was defined as the main reactivity peak for sewage sludge char combustion. The last peak was occurred around 690°C corresponding to the decomposition of the inorganic compound containing in raw sewage sludge which was not decomposed after pyrolysis [14].

The characteristic temperatures obtained from the DTG profiles for the main reactivity peak were summarized in Table 7.3. The results showed that the starting combustion temperature (T_v) shifts to higher values and the temperature of the end of the combustion (T_e) to lower ones. In consequence, the burn-out time (t_b) decreases with increasing the pyrolysis temperature at which the char prepared. For instance, the t_b of chars were in the range of 14.0-23.3 min which is comparable to the chars prepared that reported elsewhere [13]. The t_b was decreased from 23.3 min for N350 to 15.5 min for N750 or t_b was decreased by 7.8 min. Moreover, the t_b of chars prepared under CO_2 atmosphere was lower than that of chars prepared under N_2 atmosphere. For example at 750°C, t_b of C750 was shorter than that of N750 by 1.5 min.

Generally, the combustion of chars is significant by the catalytic role of metal content in raw sludge which is presented in the ash content [13, 14]. However, it might be exhibit in the same extent due to their content is greater than 60.0 wt.% in all samples. Therefore, there is no differences in the reactivity of the chars should be ascribed to this effect. Chars derived at high temperatures have higher ash content and therefore, the amount of reactive organic material is lower, which would result in a decrease in the t_b.

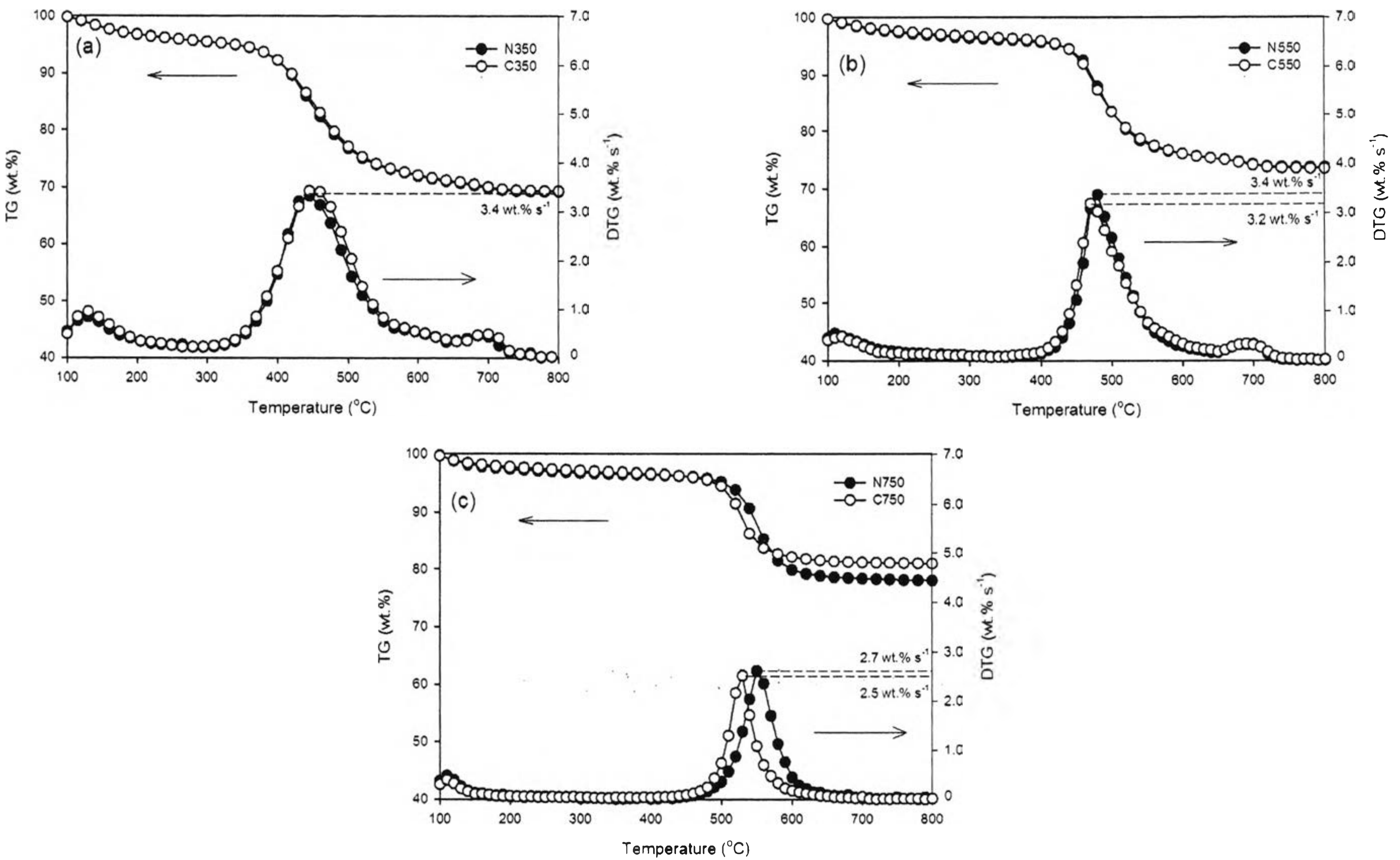

Figure 7.1 TG and DTG profiles of sewage sludge chars combustion (a) N350 and C350, (b) N550 and C550, (c) N750 and C750.

Table 7.3 Characteristic temperatures of the DTG curves and burn-out time

Sample	T_v (°C)	T_m (°C)	T_e (°C)	t_b (min)
N350	300	450	766	23.3
N450	347	455	762	20.8
N550	369	478	761	19.6
N650	380	502	730	17.5
N750	401	555	710	15.5
C350	300	455	768	23.4
C450	339	465	759	21.0
C550	362	475	752	19.5
C650	387	491	720	16.7
C750	420	528	700	14.0

[a] T_v, the starting combustion temperature (taken from at which DTG is 0.005% s^{-1}); T_m, the temperature at the maximum of DTG peak; T_e, the temperature at the end of the combustion (at which DTG is 0.005% s^{-1}); t_b, burn-out time, required time to reach complete combustion = $(T_e - T_v) \div \beta$, (β = heating rate used, 20°C min^{-1}).

R_{max} and T_m were taken to measure of the combustion reactivities of sewage sludge chars. The higher the R_{max} value the higher the combustion reactivity was obtained but the lower the T_m the more reactive a char can be considered. Figure 7.2 shows the plot of maximum reactivities (R_{max}) and T_m as a function of pyrolysis temperature for char prepared under both N_2 and CO_2 atmospheres. The results showed that the combustion reactivities of prepared chars were found to decrease as increasing the pyrolysis temperature. This is indicating by linearly decreasing in R_{max} and by linearly increasing T_m as a function of pyrolysis temperature. For example, R_{max} was decreased from 3.5 wt.% s^{-1} at 350°C to 2.7 wt.% s^{-1} at 750°C whilst T_m was increased from 449°C (at 350°C) to 555°C (at 750°C). This might be due to the decrease in the volatile matter after pyrolysis and leave the more condensed volatile structure in the prepared chars. The more condensed volatile structure, generally, is more difficult to react with air [13]. However, when the CO_2 was utilized at 350 and 550°C, there was insignificant different in reactivities, in term of T_m, of chars prepared under different atmospheres. For chars prepared at 750°C, C750 exhibited slightly higher combustion reactivity than N750. This might be due to the increase of BET surface area and total pore volume of char under CO_2 atmosphere which increases the combustion reactivities.

Figure 7.3 shows the plot of R_{max} and T_m against the BET surface area. The results showed that the relationship between reactivity and BET surface area is not a general rule, and surface area cannot be used directly as an indicator to predict the reactivity of sewage sludge chars. Figure 7.3(a), the R_m was found to rapidly decrease from 3.5 to 2.7 wt.% s^{-1} as slightly increase in BET surface area from 14 to 34 m^2 g^{-1}. For chars prepared under CO_2 atmosphere, Figure 7.3(b), R_m linearly decreased from 3.0 to 2.5 wt.% s^{-1} as increasing of BET surface area from 20.0 to 89.0 m^2 g^{-1}. For the reactivity in terms of T_m, it can be described in the opposite way to R_m. The similar findings were found for the combustion reactivities of other sewage sludge char [13], coal and synthetic coal [15].

Unlike BET surface area, total pore volume of sewage sludge char was found to increase as a function of pyrolysis temperature at which the chars prepared. Interestingly, it seems that the linear relationship can be applied for describing the decrease in R_{max} and for the increase in T_m as a function of total pore volume as shown in Figure 7.4. For example, total pore volume of chars prepared under N_2 atmosphere increased from 41 to 78 mm^3 g^{-1} as increasing of pyrolysis temperature from 350 to

750°C (Figure 7.4(a)). The increase in total pore volume was more pronounced by utilizing CO_2, Figure 7.4(b), total pore volume of chars prepared under CO_2 atmosphere was increased by 12.4% for chars prepared at 750°C. However, the linear relationship can be described R_{max} and T_m as a function of total pore volume for chars prepared under CO_2.

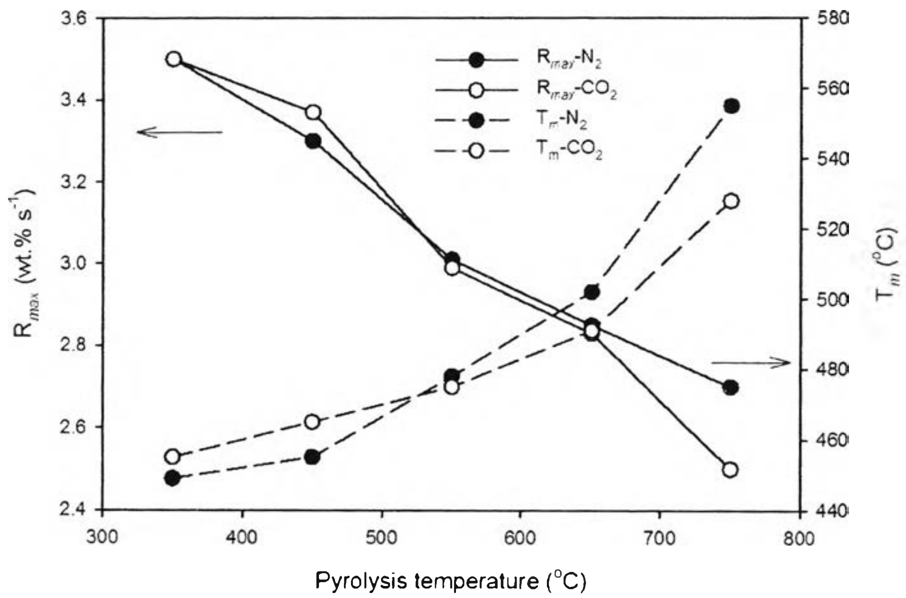

Figure 7.2 The plot of maximum reactivities (R_{max}) and temperature at the maximum (T_m) as a function of pyrolysis temperature for sewage sludge chars derived from pyrolysis under N_2 and CO_2 atmospheres.

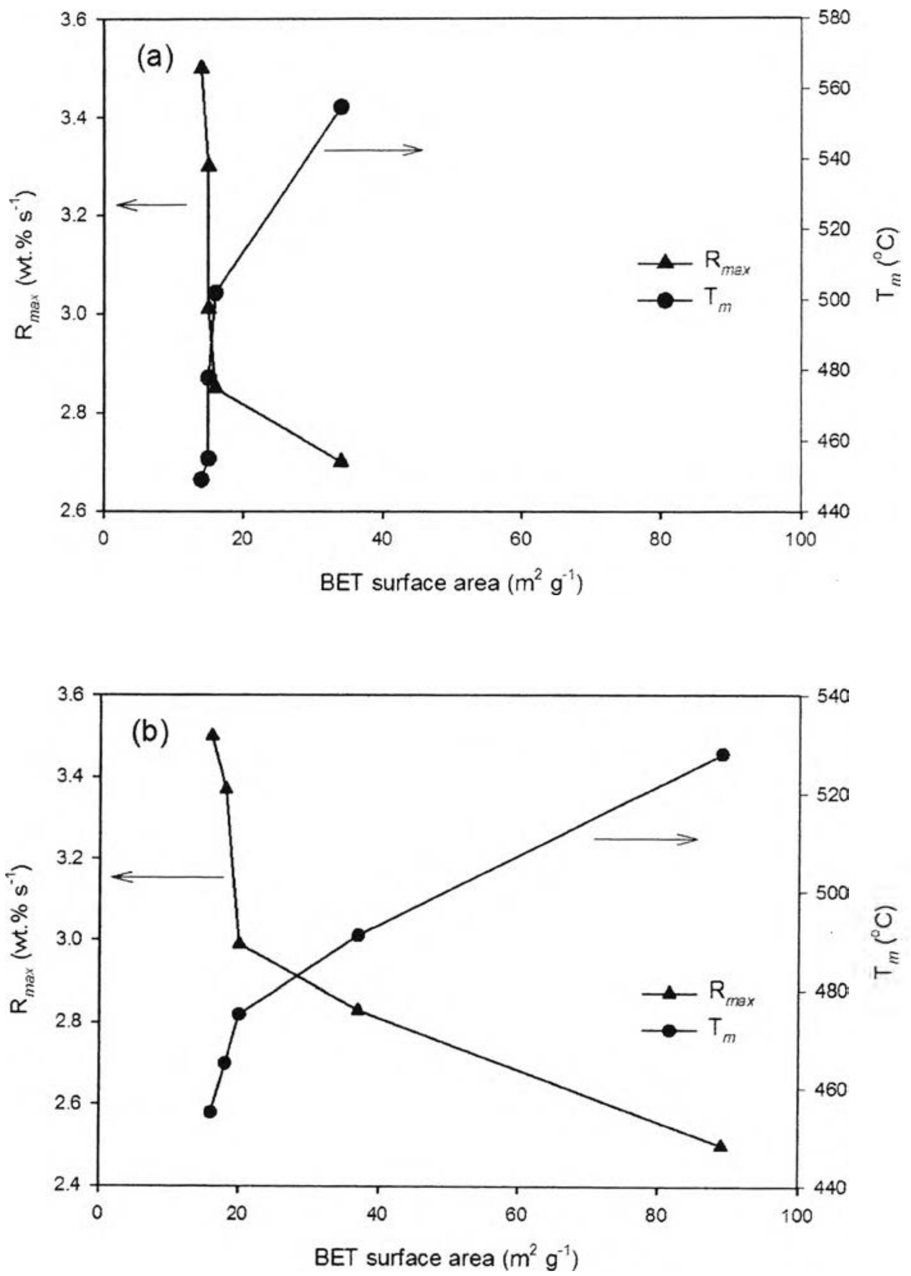

Figure 7.3 The plot of maximum reactivities (R_{max}) and temperature at the maximum (T_m) as a function of BET surface area of sewage sludge chars derived from pyrolysis under (a) N_2 and (b) CO_2 atmospheres.

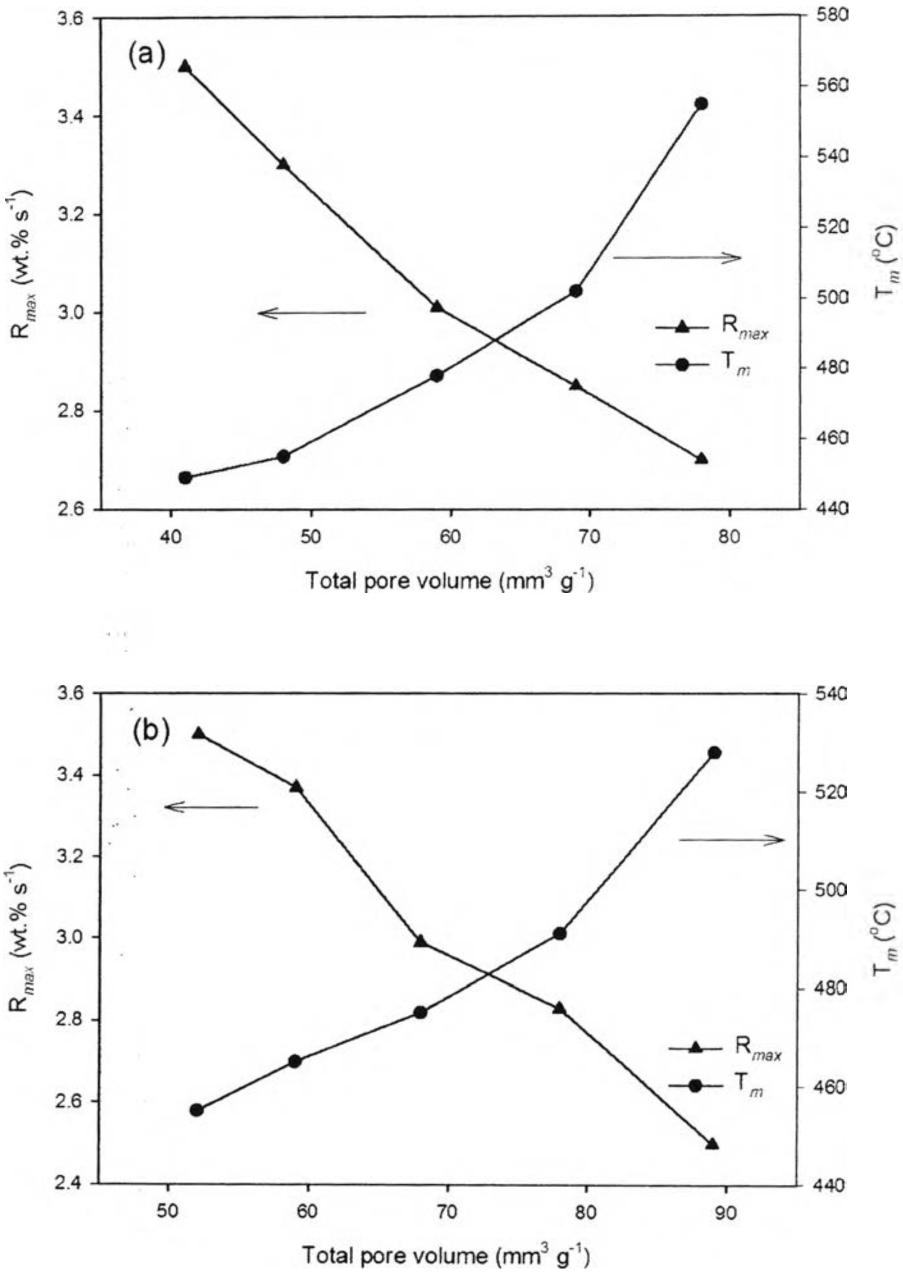

Figure 7.4 The plot of maximum reactivities (R_{max}) and temperature at the maximum (T_m) as a function of total pore volume of sewage sludge chars derived from pyrolysis under (a) N_2 and (b) CO_2 atmospheres.

7.5 Conclusion

In conclusion, the combustion reactivity of char prepared by the pyrolysis of sewage sludge strongly depends on both the pyrolysis temperature regardless of the pyrolysis atmospheres used (N_2 and CO_2) at which the chars prepared. The reactivity of all char sample becomes less reactive with the increase of pyrolysis temperature indicating by the decrease in the reactivity at the maximum (R_{max}) and by the increase in the temperature at the maximum (T_m). By utilizing CO_2 atmosphere to prepare char, there are insignificant differences on the combustion reactivity. However, BET surface area and total pore volume of chars were increased by utilizing CO_2. It was also observed that R_{max} and T_m cannot be correlated with BET surface area but R_{max} and T_m correlate can correlate well with the total pore volume. This is might be due to there is a linear relationship between pyrolysis temperature and total pore volume.

7.6 Acknowledgements

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7.7 References

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