



## Pyrolysis of oil sludge with additives of catalytic solid wastes

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### Abstract

Previous efforts have been made to convert the oil sludge into useful resources such as lower molecule organic compounds and carbonaceous residues by pyrolysis. The liquid products are close to diesel oil; however, they contain a significant amount of vacuum residues, which decrease the qualities of liquid products. For the reuse, conservation and recycling of solid wastes, the effects of using fly ash, oil sludge ash, waste DAY-zeolite and waste polymer of polyvinyl alcohol (PVA) as additives on the possible improvement of the pyrolysis of oil sludge were investigated. For the increase of conversion (X), two weight ratios of 10 and 5 wt.% additives provided the offers in the order of fly ash of 10 wt.% > PVA of 10 wt.% > oil sludge ash of 10 wt.% > DAY-zeolite of 10 wt.% > fly ash of 5 wt.% > DAY-zeolite of 5 wt.% > no additives. The addition of additives achieved the improvement of the quality (q) of pyrolysis oil (as sum of light and heavy naphtha and light gas oil) in the order of fly ash of 10 wt.% > oil sludge ash of 10 wt.% > PVA of 10 wt.% > DAY-zeolite of 10 wt.% > fly ash of 5 wt.% > DAY-zeolite of 5 wt.% > no additives. All this information is useful not only to the improvement of a pyrolysis system but also to the better utilization of liquid oil products.

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*Keywords:* Oil sludge; Fly ash; Zeolite; Ash; Polyvinyl alcohol; Pyrolysis

### 1. Introduction

For both economic and environmental reasons, energy recycling from oil sludge into fuel oils is attractive and has been commercially tested and operated. In our previous works, the

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reaction models, major products, and usage of additives of aluminum, iron, sodium, potassium and calcium compounds for the pyrolysis of oil sludge have been studied [1–7]. For the improvement of pyrolysis oil, upgrading the pyrolysis oil or adding catalysts/additives is a desirable approach. Although most expensive catalysts used can be recovered, the reuse of expensive catalysts may encounter the problem that the catalysts may be readily deactivated by sulfur poisoning at high temperature [8]. However, treatment of wastes by catalytic cracking has some advantages over thermal degradation (noncatalytic method) [9,10].

If fly ash was not properly disposed of, it would lead to environmental problems such as dusting, release of acidic substances, and pollution with heavy metals [11]. Many researchers have shown that sorbents prepared from fly ash and hydrated lime have higher SO<sub>2</sub> capture and Ca utilization than the sole hydrated lime [12–16]. Also, fly ash can be converted selectively into faujasite (Y type) zeolite and used as a catalytic material. Prashant et al. [17] pointed out that the H–Y zeolite derived from the supernatant of fly ash solution shows excellent cracking activity compared to that of standard. Other predominant and attractive aspects of catalyst usages are in the chemical recycling of waste plastics into the corresponding monomers or raw chemicals that could be reused for the production of plastics or other advanced materials. Acidic solid [18–21] (such as acidic zeolites (HZSM-5, HMOR and HUSY), non-zeolites (such as SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>) and silicalite (Si/Al >1000, siliceous analogue of ZSM-5 zeolite, mesoporous silica gel and mesoporous folded silica), metal chlorides (CuCl<sub>2</sub>·2H<sub>2</sub>O and MgCl<sub>2</sub>·6H<sub>2</sub>O), metal oxides (Al<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>, MgO and ZnO), metal acetates (Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O, Sn(OAc)<sub>2</sub>, Ca(OAc)<sub>2</sub>·H<sub>2</sub>O and Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O) [9], metal powders (Al, Zn, Fe, Ni and Cu) [22] and ceramic materials (alumina, mullite, silica and mesoporous silica (KFS-16)) [23,24] have been preferably employed as catalysts for the degradation of waste plastics. Among the immobilization techniques, poly(vinyl alcohol) (PVA) can be used to manufacture the immobilizing support of microorganisms in wastewater treatment systems. The withdrawn activated sludge contains lots of PVA. Shie et al. [25] investigated the pyrolysis of PVA. Noting that PVA consists of large amounts of OH, one may expect that the effects of OH radical on the pyrolysis of oil sludge by PVA are also interesting.

The previous studies provided some useful results of the catalytic degradation of fossil wastes. The effects of using fly ash, oil sludge ash, waste DAY-zeolite and waste polymer of PVA as additives on the possible improvement of the pyrolysis of oil sludge were investigated in the present study. The catalytic degradations of oil sludge in the presence of above additives were examined in detail. The catalytic degradation was performed by the use of a dynamic thermogravimetric (TG) reaction system at the temperature-programmed heating rate (HR) of 5.2 K/min in nitrogen atmosphere with temperatures in the range of 378–740 K.

## 2. Experimental

### 2.1. Materials

The oil sludge used in this study was sampled from the crude oil storage tank of a typical petroleum refinery plant located in the northern Taiwan. Nitrogen gas for the purge gas, with

99.99% purity, was purchased from the Ching–Feng–Harnng Co. Ltd. in Taipei, Taiwan. The oil sludge sample was dried in a recycle ventilation drier for 24 h at 378 K before use.

### 2.1.1. Thermogravimetry (TG)

The lab-scale apparatus and experimental procedures for the pyrolysis of oil sludge are the same as those in the previous studies [1–7]. The sampling and analysis may be referred to those in the previous studies [2–5].

### 2.1.2. Chemicals

The principal liquid standards for establishing calibration curve are the same as the previous study [2–6,25]. Four solid wastes were used as additives and directly added (physically mixed) into the quartz disk with oil sludge. They include fly ash, oil sludge ash, DAY-zeolite and PVA. Some chemical compositions and or physicochemical characterization of additives are shown in Table 1. Others may be referred to previous studies [6,7,25]. All of the compounds were directly used without further purification. From Table 1, main components of fly ash are SiO<sub>2</sub> (59.0 wt.%), Al<sub>2</sub>O<sub>3</sub> (26.7 wt.%), Fe<sub>2</sub>O<sub>3</sub> (5.5 wt.%), K<sub>2</sub>O (2.5 wt.%) and CaO (1.6 wt.%). Also from Table 2, main metal components of oil sludge ash are oxides of

Table 1  
The chemical compositions and properties of fly ash from boiler 3 of Shin-Da power plant of the Taiwan Power Company and of DAY-zeolite from Degussa Company

Component	Composition (wt.%)	
Chemical compositions of fly ash		
SiO <sub>2</sub>	59.0	
Al <sub>2</sub> O <sub>3</sub>	26.7	
Fe <sub>2</sub> O <sub>3</sub>	5.5	
K <sub>2</sub> O	2.5	
CaO	1.6	
TiO <sub>2</sub>	1.3	
Na <sub>2</sub> O	1.2	
MgO	0.9	
SO <sub>3</sub>	0.47	
V <sub>2</sub> O <sub>5</sub>	0.05	
Ignition Loss	2.7	
	Fly ash	Zeolite
Properties of fly ash and zeolite		
BET area (m <sup>2</sup> /g)	6.48	597.52
True density (g/ml)	2.64	2.22
Porosity	0.514	0.405
Particle size (mm)	–	0.704 (20–30 mesh)
Mean diameter D <sub>p</sub> (μm)	3.61	–
Bulk density (g/ml)	1.133	–
Micropore area (m <sup>2</sup> /g)	–	521.43
Micropore volume (cm <sup>3</sup> /g)	–	0.2423
Mesopore radius (Å)	–	53.59
Micropore radius (Å)	–	2.9567

Table 2  
Elemental analysis of initial oil sludge and solid residues of pyrolysis of oil sludge without and with additives in this study<sup>a,b</sup>

	C		H		N		C/H c	Mass ratio	
	a	b	a	b	a	b			
Initial dry oil sludge [3]	83.9 (0.90) <sup>c</sup>		12.0 (0.58)		0.81 (0.53)		6.99	100	
Without additives [3]	64.39 (0.6)		2.59 (0.06)		1 (0.04)		24.86	16.34 <sup>d</sup>	16.34 <sup>e</sup>
With 10 wt.% DAY-zeolite	31.07 (1.27)	68.49 [1.06] <sup>f</sup>	1.94 (0.007)	4.27	0.59 (0.02)	1.3	16.03	16.64	6.68
With 10 wt.% oil sludge ash	43.2 (0.37)	76.54 [1.19]	2.13 (0.19)	3.77	0.69 (0.007)	1.22	20.3	20.87	12.94
With 10 wt.% fly ash	31.71 (0.04)	65.39 [1.01]	1.93 (0.08)	3.98	0.52 (0.007)	1.07	16.43	17.65	9.38

a: based on mass of residues (including additives), units in wt.% for C, H, N; b: based on mass of oil sludge residues (with deduction of additives), units in wt.% for C, H, N; c: C/H ratio (wt./wt.) (for b column).

<sup>a</sup> Heating rate (HR) = 5.2 K/min.

<sup>b</sup> Final temperature = 740 K.

<sup>c</sup> Numbers in parentheses are standard deviations ( $\sigma_{n-1}$ ).

<sup>d</sup> Mass ratio of residues (including additives) to sum of initial dry oil sludge and initial additives added,  $M'$ .

<sup>e</sup> Mass ratio of oil sludge residues (with deduction of additives) to initial dry oil sludge,  $M$ .

<sup>f</sup> Numbers in brackets are C ratio (including additives/without additives).

Fe (Fe<sub>2</sub>O<sub>3</sub>, 36.98 wt.%), Ca (CaO, 4.89 wt.%), Na (Na<sub>2</sub>O, 1.39%), Al (Al<sub>2</sub>O<sub>3</sub>, 0.46 wt.%), Zn (ZnO, 0.44 wt.%) and Mg (MgO, 0.4 wt.%).

### 3. Results and discussion

#### 3.1. Thermal degradation of additives

In the sole pyrolysis of oil sludge, the residual mass fraction of oil sludge ( $M$ ) decreases as the thermal pyrolysis temperature ( $T$ ) increases [1]. With the addition of additive into the oil sludge, the mass residual fraction of additive ( $M_a$ ) may decrease along with that of oil sludge during pyrolysis. To clarify the actual mass loss of oil sludge only, a variation of residual mass fractions of  $M$  and  $M_a$  must be examined and compared. The  $M_a$  is expressed as

$$M_a = \frac{m_a}{m_{a0}}, \quad (1)$$

where  $m_a$  is the present mass of additive at  $T$ ,  $m_{a0}$  the initial mass of additive.

The time variations of  $M_a$  of sole additives in thermal degradation at heating rate (HR) of 5.2 K/min are shown in Fig. 1. In the thermal degradation temperature range of 378–740 K, the values of  $M_a$  of fly ash, oil sludge ash and DAY-zeolite did not have obvious reductions. However, that of PVA decreased as  $T$  increased. It is noted that samples were dried in a recycle ventilation drier for 24 h at 378 K before use. Therefore, the water content in the samples was negligible. The  $M_a$  of PVA decreased, starting at 500 K, and did not end for a constant value even at 740 K. The descend of  $M_a$  for PVA might be due to the dehydration of H<sub>2</sub>O from PVA. Shie et al. [25] pointed out that the entire pyrolysis process of PVA consists of two distinct pyrolysis stages. The corresponding activation energies ( $E$ ), reaction orders ( $n$ ) and frequency factors ( $A$ ) of the reactions of two distinct pyrolysis stages are 148.35

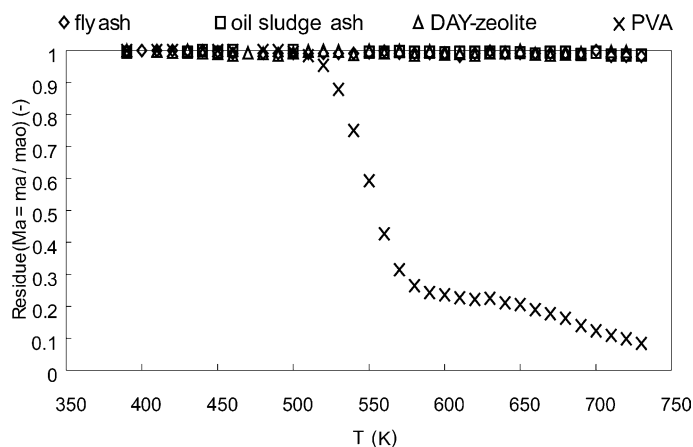


Fig. 1. Residual mass fraction ( $M_a$ ) curves of additives used in this study at 5.2 K/min heating rate. Results of PVA were from Shie et al. [25].

and 129.4 kJ/mol of  $E$ , 1.04 and 1.48 of  $n$ , and  $4.319 \times 10^{11}$  and  $5.169 \times 10^6 \text{ s}^{-1}$  of  $A$ , respectively. The curve of PVA in Fig. 1 was adopted from Shie et al. [25]

### 3.2. Effects of additives on conversion of pyrolysis of oil sludge

The oil sludge used in this study was sampled from the crude oil storage tank of a typical petroleum refinery. Its high values of combustible of 58.97 wt.% (wet basis), heating value of 10,681 kcal/kg (dry basis), low heating value of 5870 kcal/kg (wet basis) and C element of 83.94 wt.% (dry basis) suggest that the waste of oil sludge would be a valuable resource. For the sole pyrolysis of oil sludge, the major gaseous products (noncondensable gases at 298 K) are  $\text{CO}_2$  (50.88 wt.%), HCs (hydrocarbons, 25.23 wt.%),  $\text{H}_2\text{O}$  (17.78 wt.%) and CO (6.11 wt.%) [2]. The HCs mainly consist of low molecular paraffins and olefins (C1–C2, 51.61 wt.% of HCs). The distillation characteristics of liquid product (condensate of gas at 298 K) from the sole pyrolysis of oil sludge (collecting temperature range of 378–873 K) is close to diesel oil. However, it contains a significant amount of vacuum residues of about 9.57 wt.% [2]. For the reduction of vacuum residues, which affect the qualities of liquid oils significantly, lowering the reaction temperature and reusing the solid wastes, the catalytic degradation of oil sludge in the presence of waste solid additives was studied. When the mass loss of additive is considered, the residual mass fraction of oil sludge ( $M$ ) is expressed as

$$M = \frac{W}{W_o} = 1 - X, \quad (2)$$

where  $W = m - m_a$ ,  $W_o = m_o - m_{a0}$ ,  $X$  is the conversion of oil sludge,  $m$ ,  $m_a$  are the present masses of sample and additive at  $T$ , and  $m_o$ ,  $m_{a0}$  are the initial masses of sample and additive.

Fig. 2 illustrates the relation between  $M$  and  $T$  with deduction of additives  $M_a$ , for the pyrolysis systems with and without additives. It appeared that all the values of  $M$  in the presence of additives were lower than those in the absence of additives. After the temperature reached 650 K, the differences between the results with absence and in the presence of additives were more obvious. For the increases of conversion ( $X$ ), two weight ratios of 10 and 5 wt.% additives provided the offers in the order of fly ash of 10 wt.% > PVA of 10 wt.% > oil sludge ash of 10 wt.% > DAY-zeolite of 10 wt.% > fly ash of 5 wt.% > DAY-zeolite of 5 wt.% > no additives. From the orders, it showed that a higher weight ratio gave a lower value of  $M$  at the same  $T$  and thus, a higher  $X$ . Interestingly, after the temperature rose to 650 K, all the conversions with the presence of additives became higher than those without additives obviously. This might be due to the dispersion and catalyst phenomenon. Because the oil sludge is liquid type in 378–743 K [2], the additives have the dispersant effects. Sanjay et al. [26] evaluated the role of a dispersant in coal liquefaction using a mineral oil as the solvent and with different concentrations of a commercial dispersant additive (HiTEC 7049, a proprietary mixture supplied by Ethyl Corp.) added to the reaction mixture. They have pointed out that the dispersant additives presented in the waste oil were believed to enhance the coal conversion. The primary role of the dispersant additive is believed to increase coal dispersion and dissolution [26]. Further, the present results indicated that the degradation of oil sludge with additives can be carried out at a lower temperature to achieve the same degradation (conversion), in contrast to the degradation without additives. In other words, it can save the energy and treatment cost for the oil sludge pyrolysis.

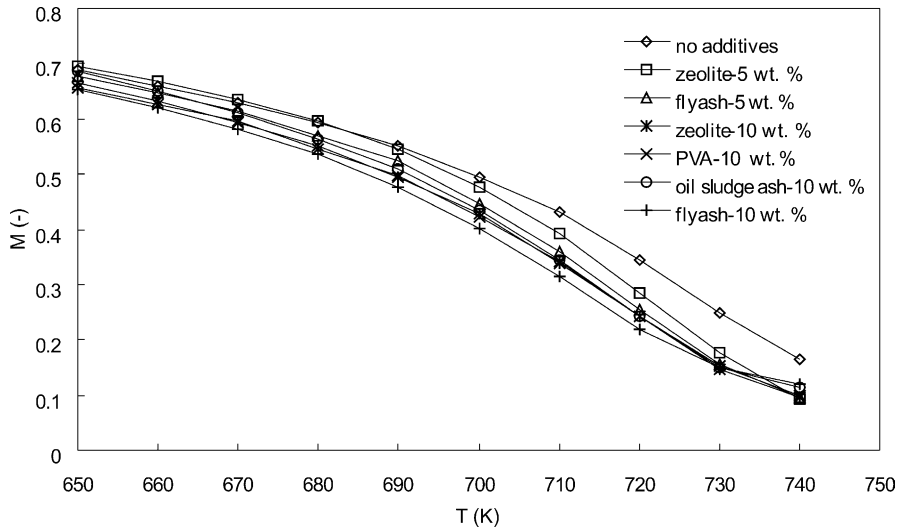


Fig. 2. Residue mass fractions ( $M = 1 - X$ ) for pyrolysis of oil sludge without and with additives at 5.2 K/min heating rate (with deduction of additives  $m_a$ ).

### 3.3. Effects of additives on reaction rates of pyrolysis of oil sludge

The variations of instantaneous reaction rates ( $r = dX/dt$ ) in the presence and absence of additives with the deductions of additives in the pyrolysis of oil sludge are

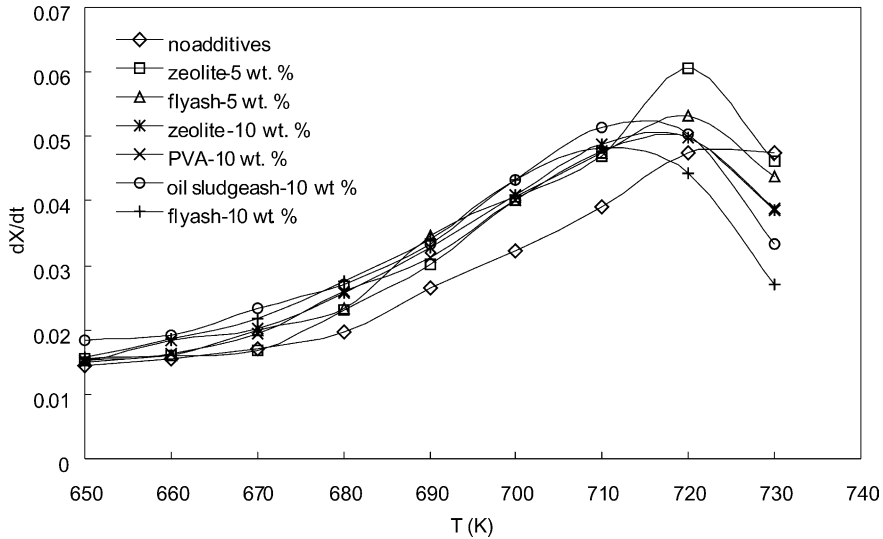


Fig. 3. Instantaneous reaction rate  $dX/dt$  vs.  $T$  at 5.2 K/min heating rate for pyrolysis of oil sludge without and with additives (with deduction of additives  $m_a$ ).

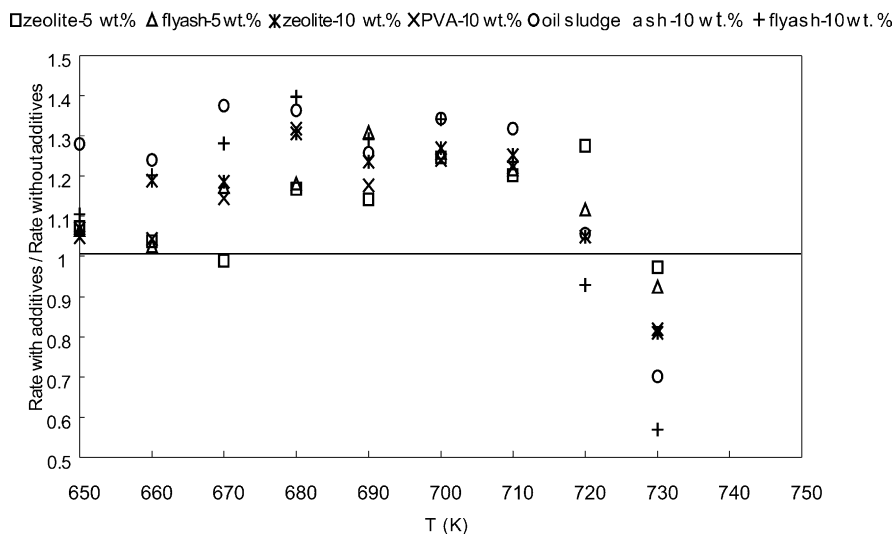


Fig. 4. Ratios of instantaneous reaction rate with and that without additives for pyrolysis of oil sludge at 5.2 K/min heating rate (with deduction of additives  $m_a$ ).

shown in Fig. 3. Their ratios ( $R_{pa} = \text{rate with additives}/\text{rate without additives}$ ) are illustrated in Fig. 4. For  $T < 650$  K, the values of  $r$  with and without additives were lower than  $0.018 \text{ s}^{-1}$  (Fig. 3). It appeared that the above additives generally enhanced the reaction rates ( $r$ ) when the temperatures ( $T$ ) were in 650–710 K, following the orders that oil sludge ash of 10 wt.% > fly ash of 10 wt.% > PVA of 10 wt.% > DAY-zeolite of 10 wt.% > fly ash of 5 wt.% > DAY-zeolite of 5 wt.% > no additives at 710 K, with the values of  $R_{pa}$  of about 0.98 to 1.4, respectively. At 720 K, the additives still enhanced the reaction rates except fly ash of 10 wt.%. However, at temperature above 730 K, the rates without additives became predominant and larger, in other words, with  $R_{pa} < 1$ . This might be possibly caused by the aggregation of additives in the solid form residues and lost of PVA after the temperature reached 730 K and consequently lost the catalyst effects. Further, the more active the additive was, the more tendency toward the lower temperature corresponding to the maximum value of reaction rate was. From these results, the favorable reaction temperature range in the presence of the additives was 650–720 K except 720 K of fly ash of 10 wt.%. The residues of pyrolysis of oil sludge were in a very high viscous form before the temperature reached 623 K (pyrolysis temperature), while low viscous or solid form after 713 K [2]. This indicated that the pyrolysis processes before 623 K might include physical volatilization with the transformation reaction (the first reaction of the three-reaction model of pyrolysis of oil sludge [1]). In the temperature range of 623–713 K, the residues of oil sludge formed aggregated solid residues (solid form) [2]. The catalysts can cause the decrease of the activation energy of the gasification of carbon [27] and lead to rate enhancement and lower the gasification temperature [28]. More in-depth study is certainly needed to understand the role of additives.



### 3.4. Influences of additives on solid residues

The residual mass fractions of sample ( $M'$ ) (without deducting the corresponding masses of additives) and oil sludge ( $M$ ) at the final pyrolysis temperature ( $T_f$ , 740 K) are shown in Table 2, where  $M' = W'/W'_0$  ( $W'$ ,  $W'_0$  are the present and initial masses of sample, respectively). Also included are the results of the elemental analysis of solid residues. It indicated that carbon (C) was the major element in solid residues. The variation of carbon element of solid residues with the additives of fly ash of 10 wt.% and DAY-zeolite of 10 wt.% relative to that without additives was not obvious. However, there was an increase of carbon element for the case with oil sludge ash of 10 wt.%. It appeared that oil sludge ash suppressed the carbon element reduction. This might be possibly caused by the aggregation of oil sludge with additive of oil sludge ash in the solid form residues. Further study would be needed to understand the cause. Also, it is noted that the C/H values were lower for DAY-zeolite of 10 wt.% of 16.03, fly ash of 10 wt.% of 16.43, oil sludge ash of 10 wt.% of 20.3 than that without additives of 24.86. The reason might be due to the inhibition reduction of hydrogen (H). The H values were higher for oil sludge ash of 10 wt.% of 3.77, fly ash of 10 wt.% of 3.98, DAY-zeolite of 10 wt.% of 4.27 than that without additives of 2.59. The same phenomenon also appeared for the pyrolysis of oil sludge with additives of CaO (3.53), CaCl<sub>2</sub> (6.72) [5], AlCl<sub>3</sub> (3.53), FeCl<sub>3</sub> (4.3) [3], NaOH (4.81), KOH (3.2), K<sub>2</sub>CO<sub>3</sub> (3.5) and KCl (3.13) [4]. The mass ratios ( $M$ ) of oil sludge residues (with deduction of additives) to initial dry oil sludge were all lower than that without additive.

In the previous studies [2,6], the results indicated that the contents of S and Cl elements in the dry oil sludge, liquid products without additives of 873 K and solid residues of 873 K are 2.06 and 0.22, 1.58 and 0.05, and 0.81 and 0.08 wt.%, respectively. The decrease of Cl in dry oil sludge in the pyrolysis temperature of 378–873 K indicates that some of the Cl reduced are condensed in the liquid products and some might be attributed to the association with of Pb to the volatilization of PbCl<sub>2</sub> (with melting point (mp) and boiling point (bp) of 771 and 1223 K) [2]. However, The contents of S elements in the dry oil sludge are almost divided into liquid products and solid residues. The examination of the influences of additives on the contents S and Cl elements in the liquid products and solid residues are not included in this study. For more detailed explanation, further researches would be needed in the future works.

### 3.5. Influences of additives on yields and qualities of liquid oils

The liquid oils were collected by passing the gaseous products through a glass connecting line wrapped with a heating tape of 410 K before collecting at 298 K. They were mostly collected in the first condensing tube immersed in 298 K water bath. The liquid yields without and with additives are expressed as

$$Y(\text{liquid yield, wt.}\%) = \frac{m_L}{W_0}, \quad (3)$$

where  $m_L$  is the total mass of collected liquids (mg),  $W_0 = m_o - m_{a0}$  (mg), and  $m_o$ ,  $m_{a0}$  (in mg) are the initial masses of sample and additives, respectively.

The liquid yields and solid residues of the pyrolysis of oil sludge without and with additives in 378–740 K are shown in Fig. 5. The liquid yield was about 69.65 wt.% with

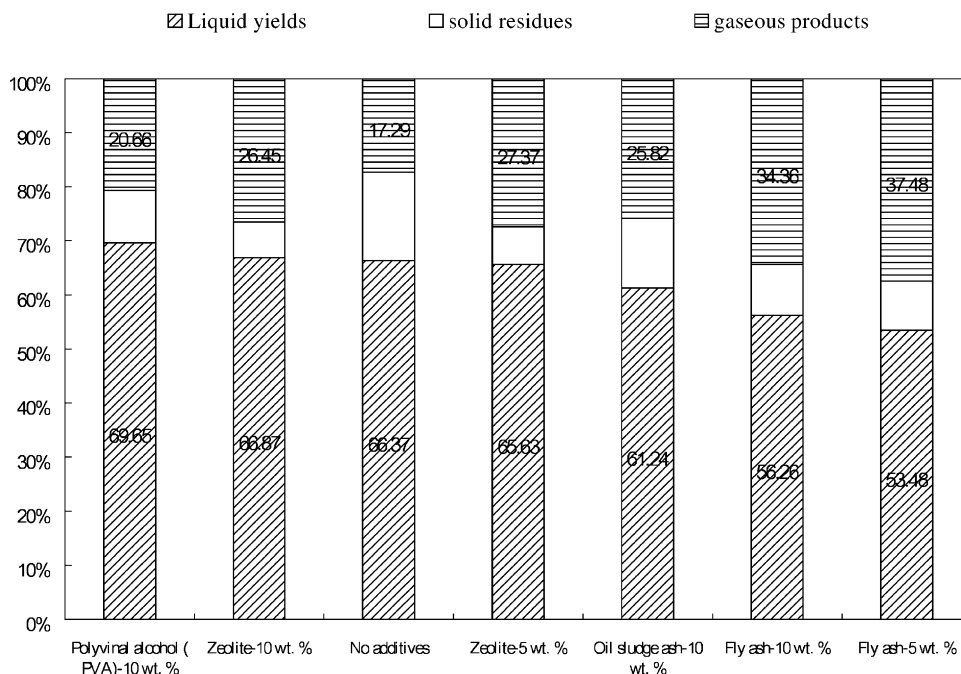


Fig. 5. Liquid yields and solid residues of pyrolysis of oil sludge without and with additives at 5.2 K/min heating rate in 378–740 K. The gaseous products are the balance.

the addition of PVA of 10 wt.%, higher than that without additives (66.37 wt.%). Nevertheless, the liquid yields with the additions of oil sludge ash of 10 wt.% (61.24 wt.%), fly ash of 10 wt.% (56.26 wt.%) and fly ash of 5 wt.% (53.48 wt.%) were lower than that without additives. This might be caused by the high activities of additives, which would effectively decompose the oil sludge producing large amounts of non-condensable gas and small amounts of condensates. The effects on liquid yields were not obvious with the addition of DAY-zeolite of 10 wt.% (66.87 wt.%) and DAY-zeolite of 5 wt.% (65.63 wt.%). Accordingly, the additives improved the liquid yields ( $Y$ ) in the order of PVA of 10 wt.% > DAY-zeolite of 10 wt.% > no additives > DAY-zeolite of 5 wt.% > oil sludge ash of 10 wt.% > fly ash of 10 wt.% > fly ash of 5 wt.%.

The liquid oils and commercial oils were analyzed at the different boiling points by GC, according to the Standard Test Method for Boiling Range Distribution of Petroleum Fractions, proposed by the ASTM D-2887 method [2]. Distillation characteristics according to the analyses are listed in Table 3. The simulated distillation results are shown in Fig. 6. The liquid oil collected in the range of 378–740 K for the pyrolysis of oil sludge without additive contained about 7.45 heavy naphtha, 43.9 light gas oil, 48.3 heavy gas oil and 0.34 vacuum residues (in wt.%), respectively. This was very similar to the fuel oil. Also, all the examined in the present study additives improved the qualities (in terms of sum of light and heavy naphtha and light gas oil) of liquid oils. The qualities of pyrolysis oil with the additives were in the order of fly ash of 10 wt.% > oil sludge ash of 10 wt.% > PVA

Table 3  
Distillation characteristics of pyrolysis oil without and with additives in this study and some commercial oils (in wt. %)<sup>a,b</sup>

	Light naphtha (343–366 K)	Heavy naphtha (366–477 K)	Light gas oil (477–616 K)	Heavy gas oil (616–811 K)	Vacuum residue (>811 K)
Without additives [3]	~0	7.45	43.9	48.3	0.34
With 5 wt.% zeolite	~0	10.51	45.21	43.79	0.49
With 5 wt.% fly ash	0.02	8.15	48.23	43.51	0.09
With 10 wt.% zeolite	2.79	7.09	46.65	43.47	0
With 10 wt.% polyvinyl alcohol (PVA)	0.19	12.43	55.01	31.87	0.5
With 10 wt.% oil sludge ash	1.27	16.56	50.72	31.45	~0
With 10 wt.% fly ash	1.16	15.83	55.32	26.21	1.49
GL <sup>c</sup>	10.07	62.93	26.15	0.85	~0
DL <sup>c</sup>	0.04	7.84	87.27	4.78	~0
FL <sup>c</sup>	~0	4.03	46.01	49.59	0.38
HL <sup>c</sup>	~0	0.29	23.88	75.19	0.64

GL, gasoline; DL, diesel oil; FL, fuel oil; HL, heavy oil.

<sup>a</sup> Pyrolysis temperature range = 378–740 K.

<sup>b</sup> Heating rate (HR) = 5.2 K/min.

<sup>c</sup> From Shie et al. [3].

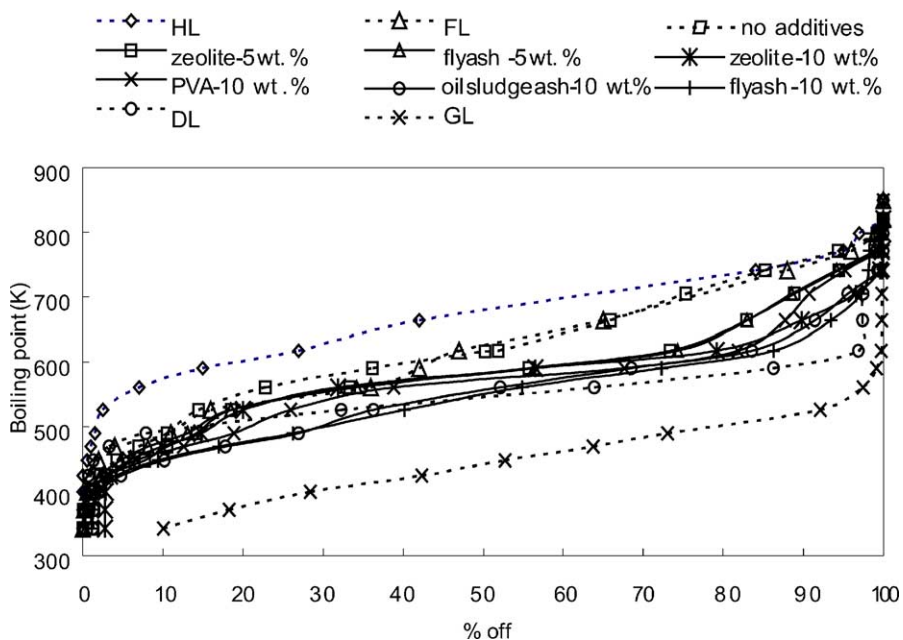


Fig. 6. Simulated distillation results of pyrolysis oil without and with additives and some commercial oils.

of 10 wt.% > DAY-zeolite of 10 wt.% > fly ash of 5 wt.% > DAY-zeolite of 5 wt.% > no additives. The qualities of pyrolysis oils with additives were all between diesel oil and fuel oil. The better quality of pyrolysis oils using fly ash and oil sludge ash might be due to their high contents of Fe (5.5 wt.%  $\text{Fe}_2\text{O}_3$  of fly ash and 36.98 wt.% Fe of oil sludge ash) and Ca (1.6 wt.% CaO of fly ash and 4.89 wt.% Ca of oil sludge ash). Shie et al. [5] pointed out that the additives achieved the improvement of the quality of pyrolysis oil in the order of  $\text{CaO} > \text{Ca}(\text{OH})_2 > \text{CaCO}_3 > \text{CaCl}_2 > \text{no additives}$ . The additive of CaO gave the best quality of liquid oil. Also, Shie et al. [3] showed that the additives of  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$  improved the qualities of liquid oils with  $\text{Fe}_2\text{O}_3$  better than  $\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ . The high activities of oxides of Fe and Ca might be due to their high dispersion in terms of active sites and can suppress the agglomeration during pyrolysis processes. Ohtsuka and Asami [28] have pointed out that the additions of CaO can improve the qualities of pyrolysis oil because of the fine CaO particles with high reactive sites. However, the clarification of exact cause of these phenomena would need more in-depth studies.

#### 4. Conclusions

The catalytic degradation of oil sludge was performed using a dynamic thermogravimetric (TG) reaction system at the temperature-programmed heating rate of 5.2 K/min in nitrogen atmosphere in the temperature range of 378–740 K. The influences of using solid wastes as additives on the pyrolysis of oil sludge were investigated in this study. The additives employed were fly ash (10 and 5 wt.%), oil sludge ash (10 wt.%), PVA (10 wt.%) and DAY-zeolite (10 and 5 wt.%). For the above additives tested, the most active additive with greatest conversion was fly ash (10 wt.%). It appeared that the above additives enhanced the values of reaction rate in the range of temperature 650–720 K. The more active the additive was, the more tendency toward the lower temperature corresponding to the maximum value of reaction rate was. However, above 730 K, the ratios of reaction rates in the presence to absence of additives ( $R_{\text{pa}}$ ) became less than 1. All the additives improved the qualities (in terms of sum of light and heavy naphtha and light gas oil) of liquid oils, with fly ash of 10 wt.% yielding the best quality of pyrolysis oil. Nevertheless, the addition of PVA of 10 wt.% resulted in the highest liquid yield. All this information is useful not only for the proper design of a pyrolysis system but also for the better utilization of liquid oil products.

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