Comparison of Calcite ($CaCO_3$) and Clay (Illite/Kaolinite) Toward the Influence of Maturation and Organic Material Potential for Processing of Oil Shale Material

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***Abstract*--** **To heat shale material on certain temperature can alter its organic compound and change it physically and chamically which then can produce energy resources such as oil and gas. Researcher has sucessfully conducted a synthesis on shale material using illite and calcite as the basis. The outcome shows that those materials are acted suitably as oil shale. SEM and XRD analysis outcome show that both shale materials have small pores because the pores cavity evenly filled by organic material, accumulated and bound strongly with illite, kaolinite or calcite, and other materials in small percentage. Moreover, the temperature to change shale material into crude oil (Tmax) on both materials is well-suited to oil shale, i.e. 421^{O}C-453^{O}C. Tmax of carbonate- organic (400^{O}C-450^{O}C) is higher than clay-organic (325^{O}C-430^{O}C). The formation of gas on carbonate-organic (T-over=750^{O}C-1000^{O}C) is higher than clay-organic (T-over=650^{O}C-900^{O}C). The outcome of TGA and Pyrolysis analysis also show similarity, i.e., all three materials have maximum maturation level on 322^{O}C, 323^{O}C, and 493^{O}C, indicating different thermal maturation level in which carbonate shale needs higher temperature and longer time than clay shale. Outcome of pyrolysis suggests clay-organic hydrocarbon has a better potential (PY=605,06-652,45 mg/g and TOC=19,94-34,38%) than carbonate-organic (PY=164,53 mg/g and TOC=9,14%). Combination between Hydrogen Index (HI) and Tmax shows clay-organic taking role as oil shale that more likely potential to be oil and gas, while carbonate-organic is not a perfect oil shale yet.**

***Index Term*--** **oil shale, clay-organic, carbonate-organic, Tmax, hydrocarbon potential**

1. INTRODUCTION

The dwindling amount of resources and the escalating price of petroleum have directed more attention to oil shale as energy source. Brendow (2003), Alali (2006), Al Hasan (2006), Peters *et al* (2005) are those who conducted research about oil shale. Based on Bartis *et al* (2005), exploitation of shale material is gathered and sent to be processed by directly burning the shale which then used as source of electrical energy. Bartis *et al* also did underground shale material mining using room and pillar mining method. Burhnham *et alI* (2006) did ex-situ process on extraction of shale material. Research on oil shale exploitation outcome combined with a huge amount of ash is conducted by Al-Hamaiedh *et al*, 2010).

Subono, Siswoyo (1995) and Dewanto (2008) has conducted research on conversion that involved heating shale material in the absence of oxygen in certain temperature until the material decomposes into gas, condensed oil and solid residue. The common temperature of this is at 842^{O}F and 932^{O}F (Youngquist dan Walter, 1998). Decomposition process was begun at relatively low temperature (300^{O}C/570^{O}F), but faster and more complete outcome produced at higher temperature (Koel and Mihkel, 1999).

Many companies possess patented method to process the shale material, but most of it are still on experimentall phase. Hundreds of patent for shale material processing thechnology have been done, but only a few of it are tested. Based on Qian and Wang (2006), there are 4 permanent technologies used for commercial, i.e., Kiviter, Galoter, Fushun and Petrosix.

Utilization of shale material is categorized as new technology and non-conventional since the process does not stop on driliing and producing oil, but one more research process is necessary to finally produce shale material. Yoshioka and Ishiwatari (2002) conducted some on going research to characterize organic material, but only a few of it specifically discuss and study about types of organic material matrix associated with clay or carbonate with heating treatment. Based on Nelson (2001), Nur (1984) and Qodari (2010), the clay material used are kaolinite $Al_2Si_2O_5(OH)_4$, Montmorillonite $Mg_2Al_{10}Si_{24}O_{60}(OH)_{12}$, Illite $K_y(AlFeMg)(Si_{2-y}Al_y)O_5(OH)$, and Chlorite $(OH)_4(Si\ Al)_8(Mg\ Fe)$. Meanwhile, carbonate materials are calcite $CaCO_3$, and dolomite $CaMg(CO_3)_2$.

Kogerman (2001) stated that research on shale oil and shale material is now a central research on Russia. The research institution is made considering the fast growing research on shale material. Berraja, Barkia, Belkbir, and Jayaweera (1988) began a research to conduct study analysis of thermal toward shale material in Tarfaya. Although the method used was not efficient, but the outcome of the research resulting an advanced theory used until today, called Pyrolysis method. This method was initiated by Katz (1983), but still revolves around on the limitation of Rock-Eval pyrolysis in analyzing organic material.

The information is then used to choose the types of material suitable for this research, i.e., material that highly affected by organic material maturation for conversion process of oil shale into hydrocarbon in form of crude oil. Maturation of organic material has different Tmax, therefore affects the duration and quality or the transformation process from oil shale into hydrocarbon in form of crude oil. Nagendrapa (2002), Cogo *et al* have conducted research about characteristic of organic material. Therefore, deeper research is necessary to study organic material lodged in clay-organic material (Illops and Killops, 2005).

Beside Tmax, it is important to know the temperature needed by water molecules to detach from crystal structure of clay and carbonate shale. Therewith, it is necessary to study the current temperature when perfect phase process is reached. This is indicated by change of structure on clay-organic and carbonate-organic material and disappearance of water molecules chemically. The last is to study the current temperature when the molecules in clay and carbonate material are detaching. Praptish *et al* (2009) have conducted research for TOC, Tmax, HI value and type of kerogen material.

2. RESEARCH METHOD

2.1 Sample Selection

Research activity is focused on characterization of clay and natural carbonate united/compacted with organic material salycilic and stearic acid. Those organic materials are chosen since the matrixs are well-suited the matrix of oil shale.

Part of shale materials, clay (illite, Kaolinite) and natural carbonate (calcite) used as organic container, prepared with petrophysical that further will be analyzed to know type and characteristic of the material.

Suitable TOC value from Waples (1985), Rachmat (2007), Widjaya *et al* (2011) and Dewanto (2013) is used as comparison and reference in the making of shale material either using clay or carbonate container.

2.2 Characterization and Test

After getting the desired organic container, the clay materials, clay-organic and carbonate-organic are placed seperately. It is stirred and pressed, then kept for 48 hours, then stirred and pressed again so that it fills all the pores in the clay container. After that, the shale materials are kept for two weeks so that the organic materials are trapped, binded and compacted. Next, using BET, the researchers measure the size of the specific surface.

The most important characteristic is that TOC of synthesized shale material should be ≥12. It shows a good nature of oil shale that can be used as comparison reference. An X-Ray Difraction (XRD) analysis is conducted to know the oxide distribution on the surface of the shale. Meanwhile, SEM analysis is conducted to know the material's morphology.

Further, Thermogravimetric Analysis (TGA) is done to measure change on weight of the compound as the function of temperature or even duration, as well as to know weight and phase change of the materials.

Pyrolysis method consists of heater (oven) at inert atmospher temperature (helium) and 100 mg sample to determine:

a. Free hydrocarbon in the samples (shale-clay, shale-carbonate, shale-oil).
b. Compound of hydrocarbon and oxygen evaporated from the beginning of cracking process of organic material in the samples (shale-clay, shale-carbonate, shale-oil).

Tmax is an indication of maturation level of organic material inside shale-clay, carbonate shale and oil shale. Tmax value is one of geochemical parameter used to determine maturation level of shale-clay, shale-carbonate, and oil shale. Termal Maturation level is measured by Tmax. For Example: if Tmax is <435 ^{O}C, it shows that shale-clay, carbonate shale and oil shale are not mature yet. If Tmax is >470^{O}C, it is over mature. Chart of pyrolysis outcome is called Pirogram and can be seen in program figure.

Research outcomes from Tobing (2003), Tjahjono (2004), Heryanto (2006) and Hermiyanto (2009) are taken as reference for processing the data from the outcome of this pyrolysis process. Then, the data will be processed further to get several lab test parameters that describe maturation and potential of some types of shale materials mentioned above, i.e., HI (Hydrogen Index), OI (Oxygen Index), PI (production index), PY (Pyrolysis Yield) and PC (Carbon Pyrolyzable.

3. DISCUSSION

3.1 SEM Analysis on Clay Material

Figure 1 shows SEM photos of clay material. Pores are filled by kaolinite and illite material (A-D, 1-6). Unstable change on particle, presence of clay material, kaolinite and unstable cumulation on material form secondary porosity.

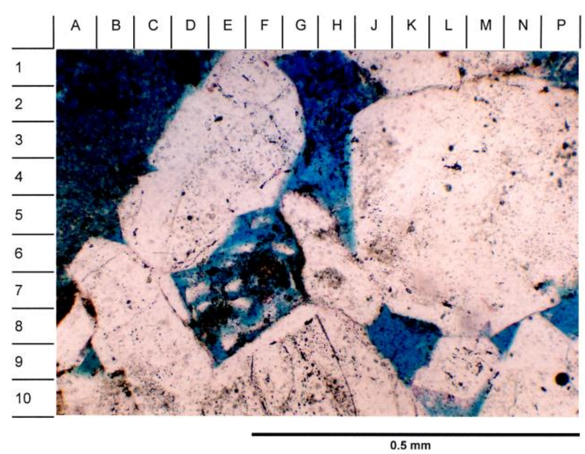

Fig. 1. SEM Analysis of Clay Material (OD2); Pores are filled by kaolinite and illite material

Clay material has a good primary and secondary porosity (20%), as good as the connexion among the pores. The improvement on porosity is mainly influenced by the detachment of stable particle (F-J, 1-5; blue color).

Figure 2 is SEM analysis outcome on clay material with 370 times magnification. It shows illite cementation that limit the development of quartz cement (C-D, 1-3; E-H, 3-5; J-L, 1-2). There is a little quartz cement compaction that causes the pores widely open, although there are illite and kaolinite. Clay material with good pores value like this will be used as organic material container and take role as place for that organic material to accumulate. The organic material is expected to occupy all existed pores, bound tightly, covered by clay and distributed evenly. Clay is expected to be catalyst on maturation process of organic material during the heating process.

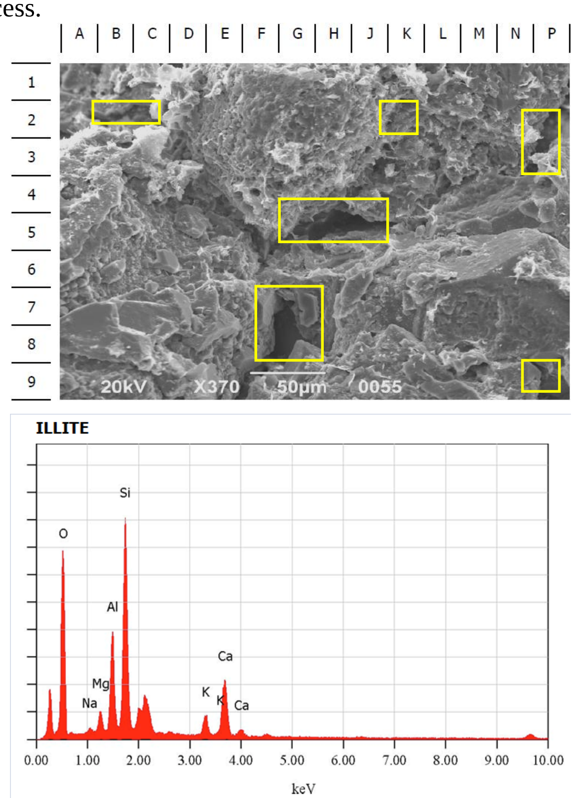

Fig. 2. SEM analysis outcome on clay material OD2 with 370 times magnification

3.2 SEM Analysis on Carbonat Material

Based on microscopic investigation, Figure 3 shows composition domination by carbonate (G-M, 1-3; A-H, 8-9), which related a bit of clay material (carbonate mud).

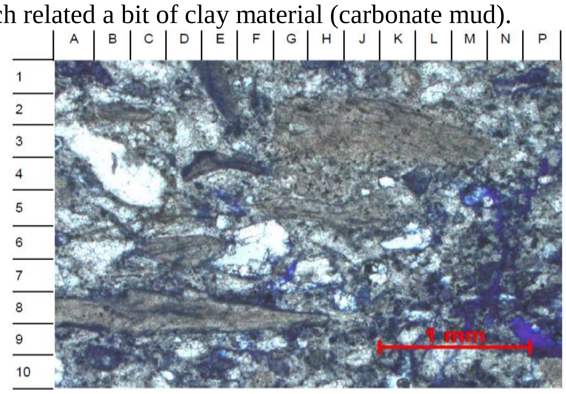

Fig. 3. The results of SEM analysis of carbonate material (OD7)

This sample experiences compaction mechanically and chemically causing sedimentary of carbonate cement. Secondary pores is produced by clay carbonate matrix. Porosity seems moderate (10,25%) and dominated by secondary pores types (blue zone) and micro porosity. The total of porosity is 1.00% and low connetion on porosity and probably only local area are well-connected.

Figure 4 shows SEM analysis outcome on carbonate material (OD7). The carbonate material (OD7) has huge amount of poressome of the space in pores can be filled by other material (C-E, 2-4). Carbonate material is dominated by calcite D-E, 2-3; B-D, 2-4) and small amount of dolomite (C-D, 5-6).

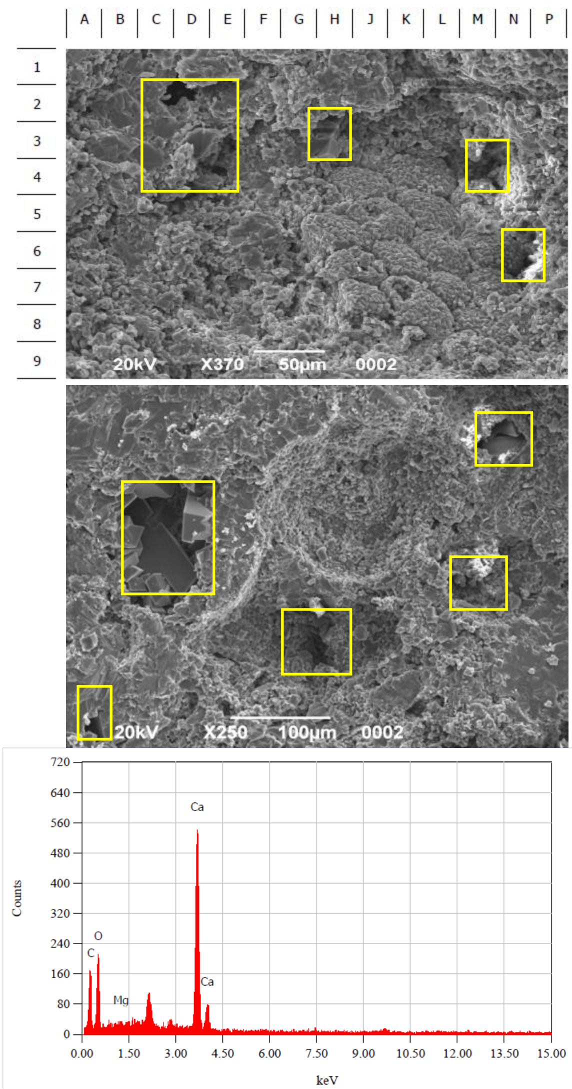

Figure 4.
The results of SEM analysis on carbonate material with a magnification of 370 times and 250 times

Figure 5 shows shale material, i.e., carbonate-organic material (OD7-Asl3). The previous research used clay container, therefore this research uses carbonate container or a place for strongly bounded organic material to accumulate.

The method of carbonate shale formation OD7-Asl3 is the same as OD2-Ast2. The difference is on the stirring. It has bigger pressure and longer duration (48 hours). The goal for the trapped organic matter (filled) pores and more binding as well as compact. Afterward, size measurement toward the surface of the shale material is taken with BET test tool. The narrowing pore that filled evenly by organic material, can be seen at SEM analysis outcome (Figure 5).

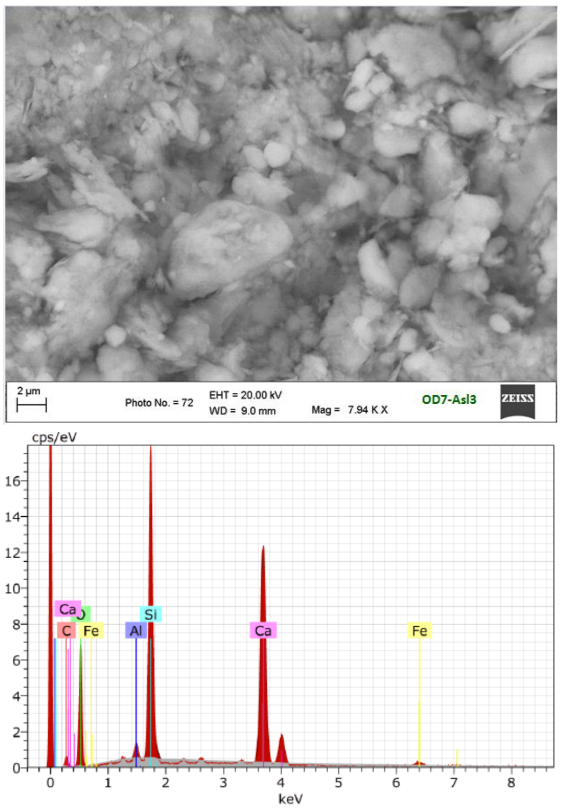

Fig. 5. The results of SEM analysis on carbonate-organic (OD7-ASL3)

SEM photos of carbonate-organic, at a glance, looks the same as clay-organic, but, in fact, there is minor different, i.e., character of carbonate material (calcite) has dominant secondary pores. The porosity will experience change at certain amount of time causing organic material or else to in and out the pores. Yet, in case of organic container, calcite can be a perfect place for maturation of organic material although it needs higher temperature as suggested by pyrolysis and TGA test.

SEM photos on organic-carbonate shows that the material is covered tightly by organic. Edax SEM outcome suggests carbonate organic contains some elements with (wt,%) as follow: Carbon (7.76%), Oxygen (62.39%), Aluminium (0.74%), Silicon (13.025), Calcium (15.59%) and Iron (0.48%).

3.3 X-Ray Difraction Measurement

Figure 6 and 7 are outcome of XRD analysis on 2theta angle 10^{O}-80^{O} on natural carbonate material, or in this case calcite ($CaCO_3$). Compared to carbonate-organic on figure 8 which is the carbonate material OD7 that is filled or bound with organic material Asl3. After having tested pyrolysis TOC values approaching 12%.

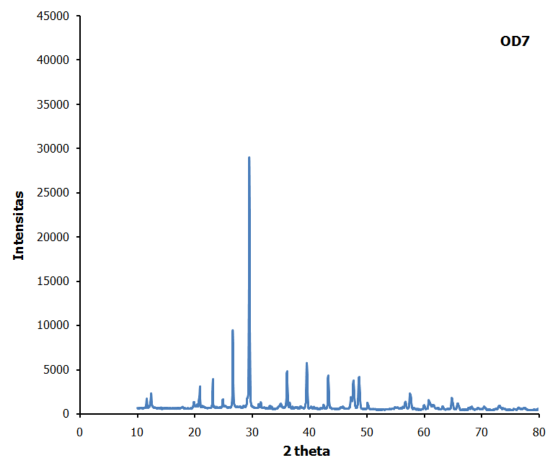

Fig. 6. Graph the results of XRD carbonate material (OD7)

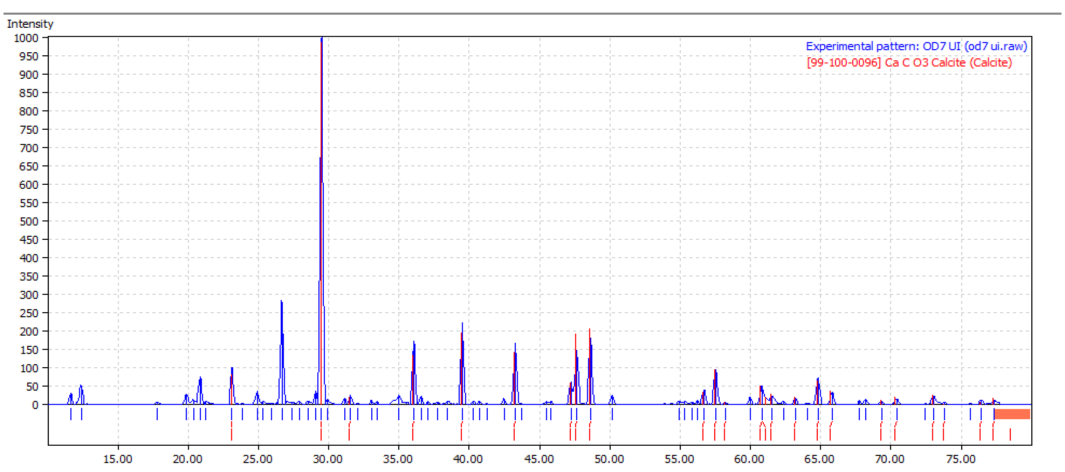

Fig. 7. Chart carbonate material, calcite (OD7) from software match

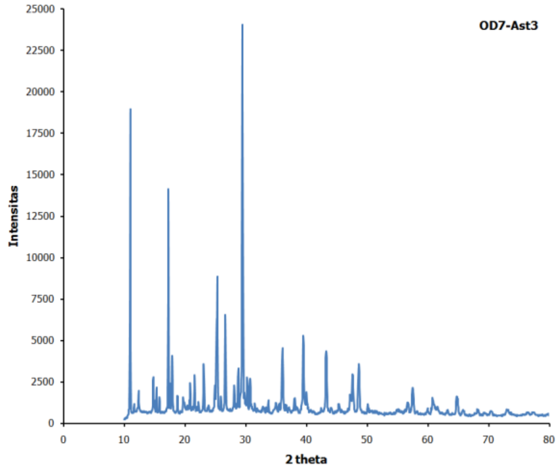

Fig. 8. XRD results of carbonate-organic (OD7-Ast3)

Figure 8 shows that peaks increase and most of them are on lower 2theta angle compared to chart on figure 6, meanwhile the magnitude of intensity experience bigger change. The narrowing of 2theta angle on several peaks indicates that pores cavity of carbonate-organic are filled and bound with organic material. Therefore, the presence calcite and illite will act as catalyst on heating and organic maturation process and expected to help conversion process of oil shale into crude oil.

3.4 TGA Analysis Outcome

TGA analysis outcome on carbonate-organic as shown at Figure 9, suggests that the last phase change happening at approximately temperature 750^{O}C. It is higher than phase change of clay-organic which is approximately 650^{O}C (Figure 10). Carbonate-organic experience 4 times weight change. First change happens at approximately 115^{O}C as water molecules inside crystal structure evaporating. At 200 ^{O}C, second change happens significantly, indicated by structure change on shale carbonate material and the loss of water molecules chemically.

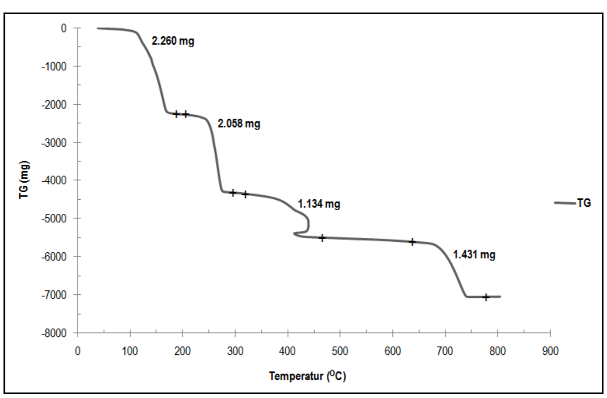

Fig. 9. Results Analysis TGA for carbonate-organic material

When calcination is conducted, another weight loss is happenning at temperature 400^{O}C, thus detachment of molecules in carbonate-organic re-occuring, which influence the change of pore size. Temperature ±(400^{O}C-450^{O}C) causes weight loss before the last loss at last temperature indicating maximum temperature needed by carbonate shale to transform into oil shale.

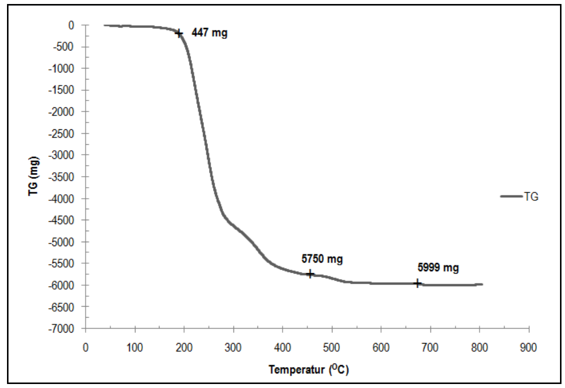

Fig. 10. Results Analysis TGA for the clay-organic material

When calcination continously done from the beginning of last loss to constant status, specifically at temperature 740^{O}C, many molecules inside carbonate-organic are detaching, as well as some parts inside the pores.

This condition is generally called as over mature (T-over), where the chart line tend to stay horizontal along with the increase of temperature up to 800^{O}C. This also indicates that the structure of material has broken and cannot be used as reference shale material anymore. More than that, physically, calcination on temperature higher than 700^{O}C changes the color of the material into blackish. Therefore, the required temperature in a process of oil shale conversion on carbonate-organic into crude oil is approximately ± 400^{O}C-450^{O}C, higher than clay-organic (Figure 10) which is on ± (325^{O}C-430^{O}C).

3.5 Testing Results TOC and Pyrolysis

Outcome of TOC test and pyrolysis on 3 samples of shale materials is available in Table I. Two clay-organic material (OD2-Ast1 and OD2-Ast2) suggests very good quality as shale material with TOC> 12,0%. Meanwhile, carbonate-organic material also shows good quality but not as good as clay-organic material. Amount of organic material on clay and carbonate is stated by total organic carbon (TOC) in percent of shale material, because TOC value is > 12.0%. This TOC value is used as one of parameter on early selection of shale material to separate low quality shale material and the good one which then used as basic processing of oil shale.

Next, raw data S1, S2, and S3 are normalized with organic carbon from shale material, resulting value in miligram per gram of TOC. The normalized value of S2 and S3 is then called as Hidrogen Index and Oxygen Index (OI). Since some variants of TOC are eliminated during measurement of normalization, therefore, HI acts as indicator of types of shale material (clay and carbonate). Later, this

Hydrogen Index needs to be corelated to effect of heating to clay shale, carbonate shale and oil shale.

Thermal maturation analysis done to these three shale materials bring about 322^{O}C, 323^{O}C, and 493^{O}C, indicating different thermal maturation level on each material, in which carbonate-organic needs higher temperature and longer time compared to clay-organic. Combination of Hydrogen Indexs and Tmax suggests that clay organic takes role as oil shale that tend to be oil and gas, while carbonate-organic is not a perfect oil shale yet.

Table I
TOC Analysis Outcome

No	No Sample	TOC (%)	S1 (mg/g)	S2 (mg/g)	S3 (mg/g)	PY (mg/g)	Tmax (^{O}C)
1	OD2-Ast1	19,94	543,66	61,40	17,32	605,06	323
2	OD2-Ast2	34,38	574,42	78,03	19,50	652,45	322
3	OD7-Asl3	9,14	141,63	22,90	37,45	164,53	493

Table II
Potential of shale material based on HI and OI

No	No Sample	HI	OI	PI	PC	Main Product	Relative Quantity
1	OD2-Ast1	308	87	0,90	50,22	Oil	Medium
2	OD2-Ast2	227	57	0,88	54,15	Oil and Gas	Small
3	OD7-Asl3	251	410	0,86	13,66	Oil and Gas	Small

Table II shows shale material potential based on HI and OI. HI is the outcome of $(S_2\times100)/TOC$ and OI for $(S_3\times100)/TOC$. The value of these two parameters will decrease along with the increase of maturation level. A high HI shows clay material is dominated by organic material or oil prone. Meanwhile, high OI value indicates the domination of gas-prone organic material. Waples (1985) research stated that HI value can be used to determine the type of main shale material and organic material produced.

Table III
Potential of shale material based on HI and OI (Waples, 1985)

HI	Main Product	Relative Quantity
<150	Gas	Small
150 – 300	Oil & Gas	Small
300 – 450	Oil	Medium
450 – 600	Oil	Ample
> 600	Oil	Plentiful

Basis to determine shale material potential is taken from previous researches that have succesfully conducted. Waples theory (1985) is taken as the basis to study the potential of oil shale material (Table III). In fact, those two shale materials have different characteristic, in which clay (illite) gives huge influence on heating and maturation process of organic material contained in OD2-Ast1 and OD2-Ast2. Meanwhile, effect of carbonate material (calcite) toward OD7-Asl3 is less visible compared to illite.

Different material effect also influences duration and value of maximum temperature needed in phase changing process as well as the detachment of water molecules and other molecules in the material. Carbonate material needs longer time and higher temperature compared to clay material (illite or kaolinite). This means clay material (illite) has stronger influence domination toward the maturation process and phase change of organic material (from TGA test outcome), than carbonate material (calcite). In other words, the outcome of pyrolysis test can be objective indicator of this research supported by outcomes of SEM characterization, XRD and TGA test.

3.6 Identification of Molecular Structure on Calcination results Shale Clay or Carbonate

Information about molecule structure can be gotten precisely and accurately on calcination outcome of clay-organic and carbonate-organic. Another advantage from FTIR measurement is that it can identify sample in various phase (gas, solid, and liquid).

Figure 11 shows FTIR measurement on outcome of clay-organic heating. Spectrum has peak characteristic around 4000 to 2500, in which well-suited to the absorption caused by NH, CH and obligation of single OH. It means that the material has C-H bound with Alkana type and has a strong intensity which fits to what is expressed by Skoog *et al* (1998). Other Spectrum has peak characteristic around 4th zones, which is 1500 to 400. Fourth zone is known as fingertip area of IR spectrum and contains most of absorption peak for various single bond.

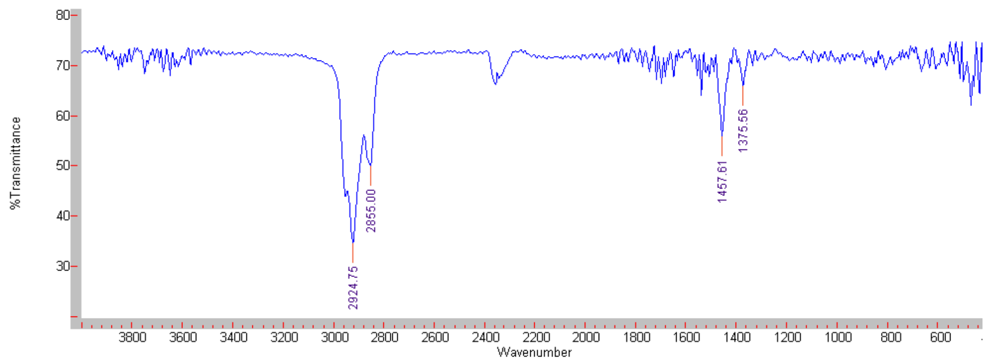

Fig. 11. FTIR measurements on heating shale clay

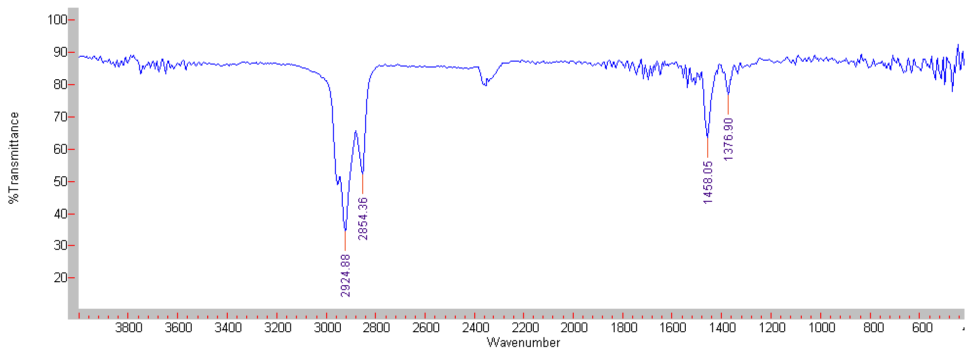

Fig. 12. FTIR measurements on heating shale carbonate

FTIR measurement on outcome of carbonate-organic heating shows at figure 12. The outcome is almost the same as clay-organic in which the spectrum has peak characteristic around 4000 to 2500 where the peak is fit to absorption caused by NH, CH and obligation of single OH. This shows that carbonate-organic has C-H bond with Alkana type and possess a strong intensity. Beside that, there is also spectrum with peak characteristic around the 4th zone, i.e., 15000 to 400. If all peaks in IR spectrum, included in fourth zone, are identical with other spectrum, hence surely that both of it are identical compounds.

4. CONCLUSION

1. The selection of shale material (OD1-Ast1, OD2-Ast2 and OD7-Asl3) has been well-suited to the characteristic of good quality oil shale, i.e., organic container from clay and carbonate with good porosity value as place for organic material to accumulate.
2. TOC value of shale material made has been well-suited the oil shale, TOC > 12%.
3. Temperature to change both materials from the shale material into crude oil (Tmax) when it has been fit as oil shale is 421^{O}C-453^{O}C.
4. TGA test suggests that clay-organic material has bigger influence in maturation process than carbonate-organic, measured by TGA test shown below:
   a. Carbonate-organic experience many phase change compare to clay-organic, so that need a longer time and higher temperature.
   b. Tmax of Carbonate-organic (400^{O}C-450^{O}C) is higher than clay-organic (325^{O}C-430^{O}C).
   c. The forming of gas on carbonate-organic (T-over=750^{O}C-1000^{O}C) is also higher than clay-organic (T-over=650^{O}C-900^{O}C).
5. Identification of molecules structure on calcination outcome of shale materials are as follows
   a. Calcination outcome of clay-organic shows the spectrum has peak characteristic at 2926.75 and carbonate- organic at 2924.88 (around 4.000 to 2.500).
   b. The peaks of both shales are suitable with absorption caused by NH, CH and obligation of single OH indicating that the shale material has C-H bond in form of Alkana type and has a strong intensity.

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