Proceedings

of

the Universal Academic Cluster

International Winter Conference

in Okinawa

February 2019

Naha, Okinawa, Japan

Universal Academic Cluster International Winter Conference in Okinawa

2 - 4 February 2019

Naha, Okinawa, Japan

International Committees

Contents

Preparation and Characterization of Tri-Sodium Phosphate Derived from Thai Monazite Ore Processing as Solid Base Catalyst

Waraporn Suksuchot[1,2, a], Dussadee Ratanaphra[3,b], Sasikarn Nuchdang[3,c] Maythee Saisriyoot[1,2,d], Penjit Srinophakun[1,2,e] and Anusith Thanapimmetha[1,2,f]
[1]Department of Chemical Engineering, Faculty of Engineering, Kasetsart University, Bangkok 10900, Thailand
[2]Center of Excellence on Petrochemical and Materials Technology, Chulalongkorn University Research, Bangkok 10330, Thailand
[3]Research and Development Division, Thailand Institute of Nuclear Technology (Public Organization), -Nakhon Nayok 26120, Thailand
[a]waraporn.suksu@ku.th, [b]dussadeer@tint.or.th, csasikarn@tint.or.th, [d]fengmts@ku.ac.th, [e]fengpjs@ku.ac.th, [f]fengjrc@ku.ac.th

Abstract

The tri-sodium phosphate compound (Na_3PO_4 compound) as the by-product of Thai monazite ore processing was used as raw material to prepare the tri-sodium phosphate dodecahydrate ($Na_3PO_4.12H_2O$) solid base catalyst. The catalyst was prepared by recrystallization method. The recrystallization of Na_3PO_4 compound with aqueous solution at different amounts (10, 32.5, 50 and 75 g in 100 g of distilled water) and crystallization times (1, 2, 4, 6, 12 and 24 h) were investigated. The prepared $Na_3PO_4.12H_2O$ catalysts were characterized by scanning electron microscope with energy dispersive spectroscopy (SEM-EDS), X-ray fluorescence (XRF) and X-ray diffractometer (XRD). The results showed that the highest yield of $Na_3PO_4.12H_2O$ catalyst was achieved under the optimum conditions: the amount of Na_3PO_4 compound of 75 g in 100 g of distilled water and the crystallization time of 1 h with the stirring rate and crystallization temperature of 600 rpm and 70 ºC, respectively. The XRF results revealed that some impurities were significantly removed. which was consistency with the SEM-EDS results. The catalyst is expected to be a promising inexpensive and reusable solid catalyst for biodiesel production.

Keywords: Biodiesel, Tri-Sodium Phosphate, Solid Base Catalyst.

Introduction

The Thailand Institute of Nuclear Technology has conducted research on the separation and purification of rare earth elements from Thai monazite ore. The monazite ore was obtained from ore dressing and tin mining in the south of Thailand (Rattanaphra *et al.*, 2019). Monazite is a rare earth phosphate mineral, $RE(PO_4)$ containing mostly light and heavy rare earth elements which is defferential atomic weight (Peelman *et al.*, 2016). The separation and purification were used alkali processing with sodium hydroxide. The tri-sodium phosphate compound (Na_3PO_4 compound) can be obtained from the reaction as shown in equation 1, which can be used as a fertilizer in agriculture. In addition, the Na_3PO_4 compound could be purified and use as solid base catalyst in transesterification.

$$REPO_4 + 3NaOH \longrightarrow RE(OH)_3 + Na_3PO_4 \quad (1)$$

Recrystallization is a purification processfor solid compound Both impurities and compound are dissolved in an appropriate solvent. This process is based on the principle that the solubility of most solids increases with increased temperature. The solubility of the compound decreases as the solution cool and crystal form (Chen *et al.*, 2016).

Several types of catalyst have been applied on transesterification -such as enzyme, ion-exchange, homogeneous and heterogeneous. The advantage of heterogeneous was insoluble in product and easily separate, therefore could be reused several times (Thinnakorn and Tscheikuna, 2014a). Jiang *et al.*, 2010 studied the transesterification of rapeseed oil with methanol using sodium phosphate as solid catalyst. It was found that the biodiesel yield of95% was achevied under the optimal conditions: mass ratio of catalyst to oil of 3%, molar ratio of methanol to oil of 9:1, reaction temperature of 70 ^{o}C and rotation speed of 600 rpm for 20 minutes.

In this study, the tri-sodium phosphate dodecahydrate ($Na_3PO_4.12H_2O$) solid base catalyst was prepared by the recrystallization method.The effect of amount of tri-sodiun phosphate compound and crystallization time on the yield of $Na_3PO_4.12H_2O$ were investigated. The prepared $Na_3PO_4.12H_2O$ was characterized by various tecniques.

Experiment

Material. The tri-sodium phosphate compound was received from Thailand Institute of Nuclear Technology (TINT). Anhydrous tri-sodium phosphate was analytical grade, purchased from Alfa Aesar.

Catalyst preparation. Tri-sodium phosphate was preparaed by recrystallization method (Huang and Logé, 2016) with aqueous solution. Different amounts of tri-sodium phosphate compound (10, 32.5, 50 and 75 g) were dissolved in 100 g of distillate water at 70 ^{o}C. The insoluble was removed using the paper filtration with vacuum pump. After that, the solution was crystallized at room temperature for 1, 2, 3, 4, 5, 6, 12 and 24 h. The tri-sodium phosphate dodecahydrate was separated from solution using the paper filtration with vacuum pump. Finally, the tri-sodium phosphate dodecahydrate was dried at 105 ^{o}C overnight to remove an excessive water.

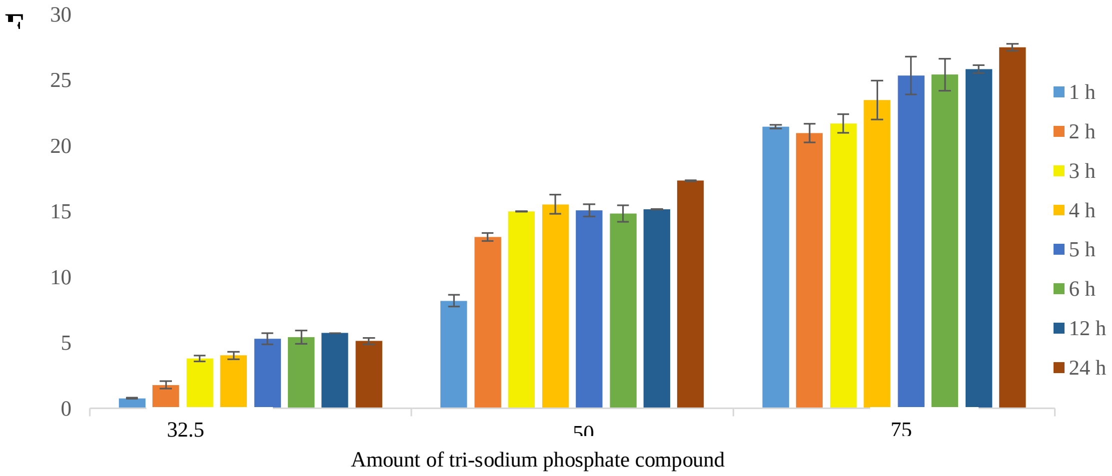
Catalyst characterization. The morphology and element contents of catalyst were observed by Quanta 450 FEI scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) at room temperature. The catalyst was coated with gold by a Sputtle Coater. The X-ray fluorescence (XRF) determined element content. The crystalline properties of catalyst was determined by X-ray diffractometer (XRD) which Cu-Kα radiation over a 2θ range of 10^{o} -80°.

Results and Discussion

Effect of the amounts of tri-sodium phosphate compound on yield of $Na_3PO_4.12H_2O$ catalyst. The effects of s amounts of tri-sodium phosphate compound in the range of 32.5-75 g on yield of $Na_3PO_4.12H_2O$ were investigated. The results are shown in figure 1. It was found that the amounts of tri-sodium phosphate compound had an effect on the yield of $Na_3PO_4.12H_2O$. An increase in the amount of tri-sodium phosphate compound increased proportionally the yield of $Na_3PO_4.12H_2O$.

Effect of the creytallazation times on yield of $Na_3PO_4.12H_2O$ catalyst. It can be seen from figure 1 that a significant increase of yield of $Na_3PO_4.12H_2O$ was observed when the crystallinzation time increased from 1 to 5 h for the amount of tri-sodium phosphate compound of 32.5 g and 75 g, from 1 to 4 h for the amount of tri-sodium phosphate compound of 50 g. However, an increase in the crystallinzation time from 5 to 12 h did not affect the yield of $Na_3PO_4.12H_2O$ for the amount of tri-sodium phosphate compound of 32.5 g and 75 g. While this phenomenon was found at the crystallinzation time from 4 to 12 h for the amount of tri-sodium phosphate compound of 50 g. Further increase in the crystallinzation time to 24 h caused in decreasing of $Na_3PO_4.12H_2O$ yield for the tri-sodium phosphate compound of 32.5 g wherase incrasing of the $Na_3PO_4.12H_2O$ yield was observed for for the tri-sodium phosphate compound of 50 and 75 g.

It can be concluded that the highest yield of $Na_3PO_4.12H_2O$ was achieved at 5 h 3 h and 1 h for tri-sodium phosphate compound of 32.5, 50 and 75 g which were 5.32, 15.01 and 21.46, respectively. At tri-sodium phosphate compound of 100 g the recrystallization could not be occurred due to the concentration was lower than solubility point of solution.



ig Pe e yi (N P(1: 2' at diffe rent amo unts of tri-sodium phosphate compound and crystallization times.

Catalyst characterization. The SEM images of $Na_3PO_4.12H_2O$ at different amounts of tri-sodium phosphate compound are shown in figure 2. The results showed that the average particle size of $Na_3PO_4.12H_2O$ catalysts were found to be around 4 µm with a rough surface for all samples.

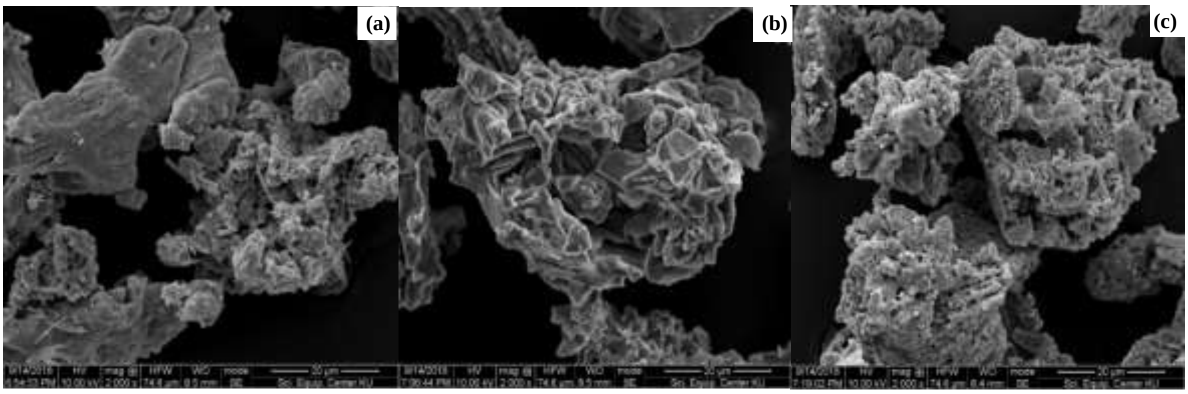


Figure. 2 SEM images of $Na_3PO_4.12H_2O$ by recrystallization method at different amounts of tri-sodium phosphate compound: (a) 32.5 g, (b) 50 g and (C) 75 g.

The elemental contents of $Na_3PO_4.12H_2O$ catalyst were evaluated by EDS technique and the results are shown in figure 3. The amount of tri-sodium phosphate did not affect the element content of $Na_3PO_4.12H_2O$ catalyst. The catalysts mainly composed of sodium phosphate.

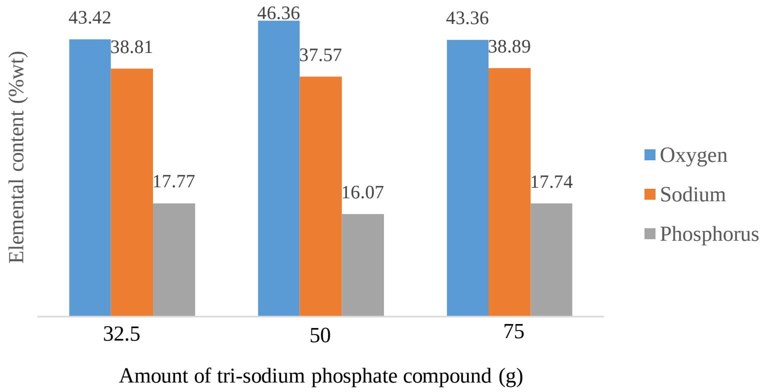


Fig.3 Elemental contents (%wt) of $Na_3PO_4.12H_2O$ determined by SEM-EDS.

The results of XRF analysis confirmed that all the tri-sodium phosphatecompound did not influence the elemental content of the solid catalyst as illustrated in figure 4. No difference in the content of sodium, phosphorus and other elements in $Na_3PO_4.12H_2O$ catalyst and the $Na_3PO_4.12H_2O$ analytical grade was observed. This result revealed that some impurities were significantly removed. In addition, these results were consistency with the SEM-EDS results.

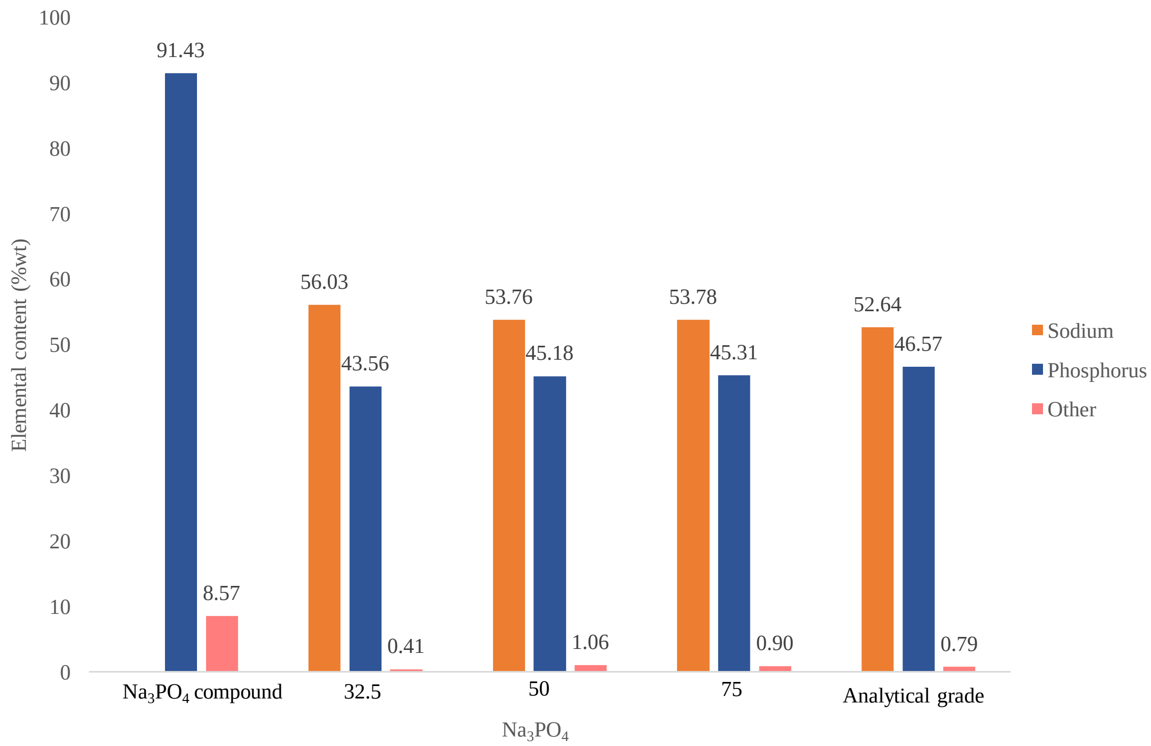


Fig.4 Elemental contents (%wt) of $Na_3PO_4.12H_2O$ determined by XRF

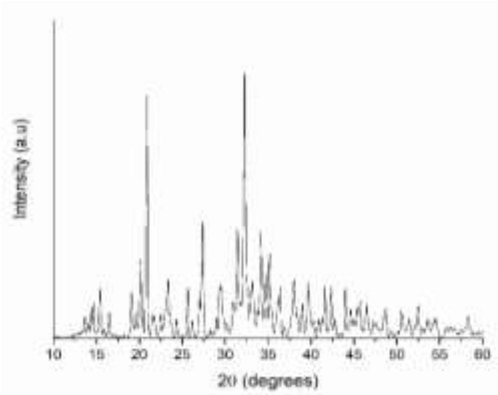


Fig.5 XRD pattern of $Na_3PO_4.12H_2O$ prepared by the recrystallization mrthod using the tri-sodiium phosphate compound of 75 g and the recrystallization time of 1 h

Figure 5. shows the XRD pattern of $Na_3PO_4.12H_2O$ prepared by the recrystallization mrthod using the tri-sodiium phosphate compound of 75 g and the recrystallization time of 1 h. catalyst. All the diffraction patterns matched well with the tetragonal phase of $Na_3PO_4.12H_2O$ compound.

From all results, it can be concluded that the optimum conditions for preparing $Na_3PO_4.12H_2O$ catalyst were the tri-sodium phosphate compound of 75 g and the crytallzation time of 1 h, the stirring rate of 600 rpm and the crystallization temperature of 70 ^oC. The prepared catalyst will be further used to study the catalytic performance in transesterification. This solid base catalyst is inexpensive, insoluble in methanol and oil, high activity. In addition, it is environmentally friendly manner because of the catalyst can easily be separated from the product by filtration or centrifuge. Morover, this catalyst has been reported that had high stability for transesterification (Thinnakorn and Tscheikuna, 2014b).

Summary

Tri-sodium phosphate dodecahydrate ($Na_3PO_4.12H_2O$) was prepared by recrystallization method. The optimum conditions for recrystallization were found to be 75 g of Na_3PO_4 compound in 100 g of distilled water and crystallization time of 1 h with the stirring rate and crystallization temperature of 600 rpm and 70 ºC, respectively. It gave the highest yield of 21.46 g of $Na_3PO_4.12H_2O$. The $Na_3PO_4.12H_2O$ is the white crystals, the average particle size of 4.17 µm with a rough surface.The prapred $Na_3PO_4.12H_2O$ is expected to be a potential solid base catalyst for transesterification.

Acknowledgement

The author would like to thank Department of Chemical Engineering from Kasetsart University. The graduate school from Kasetsart University and Center of Excellence on Petrochemical and Materials Technology (PETROMAT) for the financial support. Thailand Institute of Nuclear Technology (TINT) is gratefully acknowledged for supporting the tri-sodium phosphate compound as raw material and equipment.

References

Chen, M., L. Lin, Y. Zhang, S. Wu, E. Liu, K. Wang, J. Wang and J. Gong. 2016. Mechanism and Inhibition of Trisodium Phosphate Particle Caking: Effect of Particle Shape and Solubility. **Particuology**. 27(115-121.

Huang, K. and R.E. Logé. 2016. A Review of Dynamic Recrystallization Phenomena in Metallic Materials. **Materials & Design**. 111(548-574.

Peelman, S., Z.H.I. Sun, J. Sietsma and Y. Yang. 2016. Chapter 21 - Leaching of Rare Earth Elements: Review of Past and Present Technologies, น. 319-334. ใน I. Borges De Lima and W. Leal Filho, eds. **Rare Earths Industry.** Elsevier, Boston.

Rattanaphra, D., P. Soodjit, A. Thanapimmetha, M. Saisriyoot and P. Srinophakun. 2019. Synthesis, Characterization and Catalytic Activity Studies of Lanthanum Oxide from Thai Monazite Ore for Biodiesel Production. **Renewable Energy**. 131(1128-1137.

Thinnakorn, K. and J. Tscheikuna. 2014a. Biodiesel Production Via Transesterification of Palm Olein Using Sodium Phosphate as a Heterogeneous Catalyst. **Applied Catalysis A: General**. 476(26-33.

Thinnakorn, K. and J. Tscheikuna. 2014b. **Transesterification of Palm Olein Using Sodium Phosphate Impregnated on an Alumina Support.**

Added Value of Jatropha oil: Bio-lubricant

Kritpornpawee Pindit[1,2], Anusith Thanapimmetha[1,2], Maythee Saisriyoot[1,2] and Penjit Srinopakun[1,2,*]

[1]Department of Chemical Engineering, Faculty of Engineering, Kasetsart University, Bangkok 10900, Thailand

[2]Center of Excellence on Petrochemical and Materials Technology, Chulalongkorn University Research Building, Bangkok 10330, Thailand

[a]kritpornpawee.pi@ku.th, [b]fengjrc@ku.ac.th, [c]fengmts@ku.ac.th, [d,*]fengpjs@ku.ac.th

Abstract

Adding the value of products from non-edible Jatropha oils and Palm fatty acid distillate (PFAD), by-product of palm oil refining, were considerable. In the research, Jatropha fatty acid was modified the chemical structure to bio-lubricant base stocks to improve the physicochemical and lubricant properties. Therefore, the modification methods; epoxidation, oxirane ring opening and esterification were used to produce unsaturated fatty acid based ester derivatives. Raw materials and synthesized products were characterized using GC and NMR. Furthermore, the lubricant properties; kinematic viscosity, viscosity index and oxidative stability were evaluated followed as the standard ASTM methods and compared with lubricant specifications. The result exhibited that these derivatives had significant potential to be used as bio-lubricant base stocks.

Keywords: Jatropha oil, Palm fatty acid distillate, bio-lubricant basestocks, chemical modification

Introduction

Most lubricants derived from petroleum stock, which is toxic to the environment and difficult to disposal (Adhvaryu *et al.*, 2005). Therefore, the use of vegetable oils for bio-lubricant synthesis has many advantages including inherent biodegradability and limited toxic and and considered as potential substitutes for mineral oil-based lubricants and synthetic esters (Hwang and Erhan 2001).

Vegetable oils are convenient raw materials for use as a renewable resource and are being applied in many industry sectors such as lubricants, fuels, detergents and solvents (Bart *et al.*, 2013). However, vegetable oils are not directly suitable for lubrication application due to they have structural defects. In particular, the unsaturated fatty acid compositions of vegetable oils are poor oxidation stability (Fox and Stachowiak, 2007). Therefore, modification of triglycerides will help build molecules with desirable properties for lubricant applications (McNutt and He, 2016).

The properties of triglyceride oils can be improved in various ways such as blending, genetic modification and chemical modification (Jayadas and Nair, 2006). Chemical modification is necessary to improve certain performance limitations of triglyceride without imparing their excellent tribological and environmentally friendly property (Madanhire and Mbohwa, 2016). Table 1 showed the influene of modified chemical structure on physical and chemical properties of vegetable oil. Reactions at the double bonds could increase the product stability and ageing resistance. At the same time, the adding of polarity or functional groups and branching improves low-temperature behavior and hydrolytic stability. Thus, the modification of vegetable oil or fatty acid structure will consider the following criteria:

performance (tribological properties), thermal and oxidation stability, low-temperature behavior, biodegradability and cost.

Table 1 Influene of modified chemical structure on physical and chemical properties

Chemical modification	Properies	
	Advantages	Disadvantages
High degree of branching	Load-carrying capacity Pour point (decrease) Oxidation stability Thermal stability	Tribofilm adhesion
High linearity	Viscosity Viscosity index	Pour point (increase) Oxidation stability
High functional groups and polarity	Viscosity Tribofilm adhesion	Pour point (increase) Thermal-oxidation stability Chemical wear
Low saturation	Tribofilm adhesion Oxidation stability Thermal stability	Pour point (increase)

Chan *et al.* (2018)

The purpose of this work is to modify a structure of Jatropha oil into ester compounds with multiple reactions; hydrolysis, epoxidation and esterification for the preparation of bio-lubricant basestock using Jatropha oil and Palm fatty acid distillate (PFAD) as a precursor and to study the properties of synthetic bio-lubricants.

Materials and methods

Materials. The Jatropha oil was received from Center of Excellence for Jatropha (COE). The Palm fatty acid distillate (PFAD) was received from Patum Vegetable Oil Co., Ltd. Ethanol, hydrochloric acid, hydrogen peroxide, hiethyl ether and hulfuric acid were obtained from Qrec (AR grade). Hexane was obtained from Macron (AR grade). Sodium sulfate anhydrous was obtained from Kemaus (AR grade). Potassium hydroxide and sodium chloride were obtained from Ajax (AR grade). Formic acid was obtained from Fisher (AR grade). Sodium bicarbonate was obtained from JR F&B. Para-toluenesulfonic acid was obtained from Sigma-Aldrich Ajax (AR grade). Toluene was obtained from VWR (AR grade) and 2-ethylhexanol was obtained from Alfa Aesar (AR grade).

Preparation of Jatropha fatty acid. Free fatty acids from Jatropha oil was prepared according to the method of Salimon *et al.* (2011). Jatropha oil 50 g was saponified by refluxing for 2 h at 60^{o} C with 300 ml 1.75 M KOH in 95% ethanol. After the saponification, 200 ml distilled water was added to the mixture and the unsaponifiable matter was extracted by hexane. The aqueous layer (saponified matter) was then releasing FFA by acidification to pH = 1 with 6N HCl. The mixture was transferred to separatory funnel and the lower layer was removed. The hexane layer (contain free fatty acids) was washed with distilled water to neutral pH, dried with anhydrous sodium sulphate and the solvent removed in a vacuum rotary evaporator. The FFA% (Free fatty acid) was measured by titration followed as the standard AOCS 5a-40 methods and the fatty acid composition of Jatropha fatty acid was determined using GC-FID followed as the standard AOAC 969.3 Official methods.

Epoxidation of Jatropha fatty acid. The epoxidation method was prepared according to Hong *et al.* (2015). Jatropha fatty acid (1) 40 g and formic acid 7 ml were added in the reactor and stirred for 30 min at room temperature. 30% Hydrogen peroxide solution 38 ml was added slowly to the mixture by dropwise. At the end of hydrogen peroxide addition, the temperature was slowly raised to 70^{o} C and the reaction was continued stirring further for 5 h. After that, the mixture was transferred to separatory funnel and extracted with diethyl ether. The epoxidized Jatropha fatty acid that remained in the organic phase was washed with 5 wt% sodium bicarbonate solution, distilled water and 5 wt% sodium chloride solution in sequence. The organic layers were dried with anhydrous sodium sulphate, removed solvent in a vacuum rotary evaporator. The conversion of double bonds of Jatropha fatty acid was measured and epoxidized Jatropha fatty acid can be analyzed by ^{1}H-NMR.

Ring-opening reaction of epoxidized Jatropha fatty acid. The epoxidation method was used according to Salih *et al.* (2013). Palm fatty acid distillate (PFAD) 10 g was slowly added to a mixture of epoxidized Jatropha fatty acid (2) 25 g and p-toluenesulfonic acid (p-TSA) 4 g in toluene at 70^{o} C and refluxed for 1.5 h. After that, the temperature of reaction heated to 100^{o} C and refluxed for 3 h. After the reaction was complete, the mixture was cooled down to room temperature and stirred overnight. The mixture was washed with distilled water to neutral pH, dried with anhydrous sodium sulphate and the evaporated in a vacuum rotary evaporator to remove toluene.

Esterification of ring-opening epoxidized Jatropha fatty acid product. The esterification method was used according to Salimon *et al.* (2012). The reaction scheme for the formation of the esters as shown in Fig 1. Sulfuric acid (10 mol%) was added to a stirred of ring-opening epoxidized Jatropha fatty acid product (3) 15 g in 2-ethylhexanol 5 ml at 60^{o} C and refluxed for 10 h. Then, Hexane was added in the mixture and washed with 5 wt% sodium bicarbonate solution, distilled water and 5 wt% sodium chloride solution in sequence. Next, dried with anhydrous sodium sulphate and removed hexane in a vacuum rotary evaporator.

Results and discussion

In this work, the modification of Jatropha oil was carried out in four steps as shown in Fig 1. Starting with hydrolysis or saponification of Jatropha oil into Jatropha fatty acid using potassium hydroxide as catalyst in ethanol solution and the FFA% was determined according to AOCS 5a-40 standard. The results showed that FFA% of hydrolyzed Jatropha oil would increase from 6.24% to 98.29%.

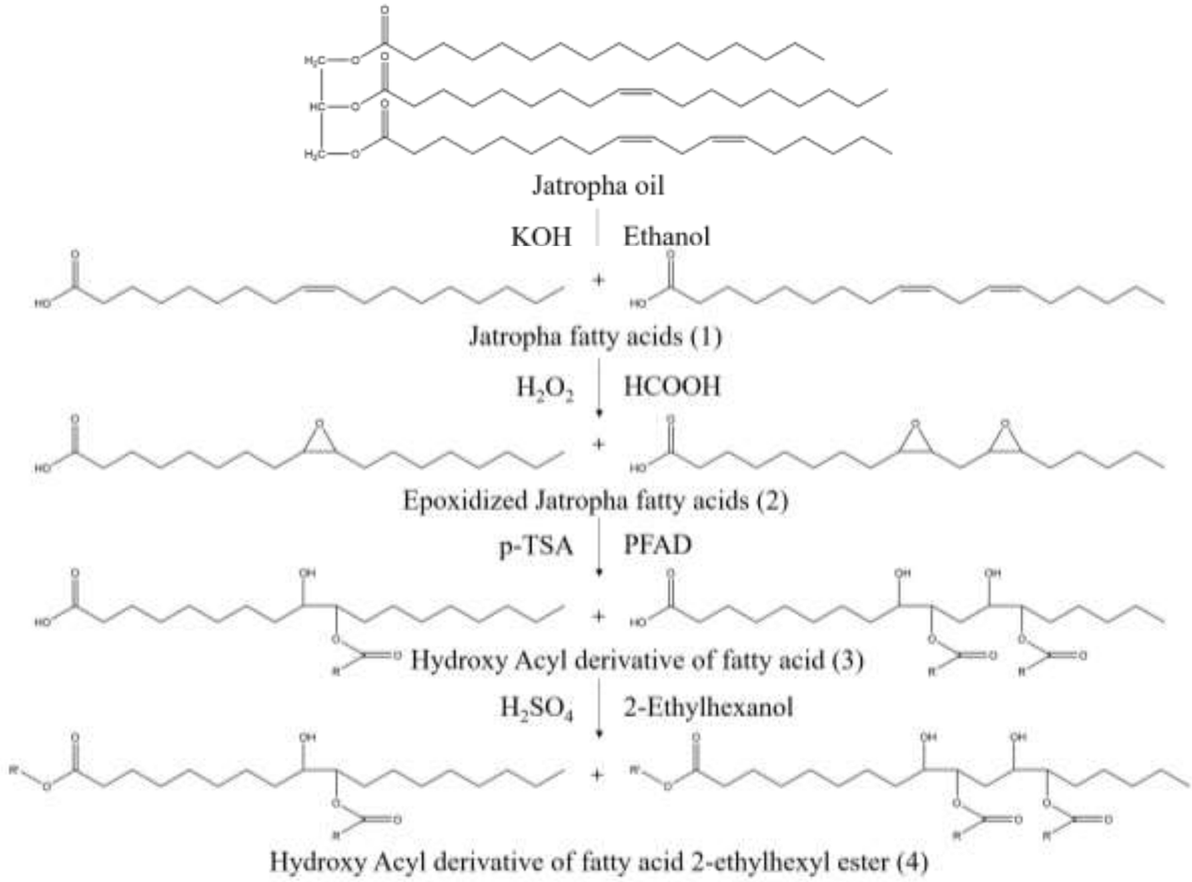


Fig 1. The reaction scheme for modification of Jatropha oil.

The fatty acid composition of Jatropha fatty acid (1) was determined using GC-FID followed as the standard AOAC 969.3 Official methods and Table 2 showed the fatty acid composition (wt%) of Jatropha oil (before hydrolysis) and Jatropha fatty acid (after hydrolysis).

Table 2 Fatty acid composition (wt%) of Jatropha oil (JO), Jatropha fatty acid (JFA) and Palm fatty acid distillate (PFAD)

Samples	**Fatty acid composition (wt%)**										
	12:0	14:0	16:0	16:1	18:0	18:1	18:2	18:3	20:0	22:1	24:0
JO	-	0.05	13.44	0.62	7.06	48.40	29.88	0.20	0.26	0.04	0.05
JFA	-	0.05	13.47	0.61	7.07	48.42	29.89	0.18	0.26	-	0.05
PFAD	0.30	1.02	44.86	0.14	4.22	39.57	8.67	0.32	0.32	0.13	0.45

The second step of modification of Jatropha oil was epoxidation with formic acid and hydrogen peroxide. The epoxidized jatropha fatty acid (2) could be analyzed by ^{1}H-NMR as shown in Fig 3 and 4. Equation 1 has been used to determine the reaction conversion of double bonds of Jatropha fatty acid and the results showed that the conversion of double bonds of Jatropha fatty acid was equal to 96.47%.

$$X\ (\%) = 100\left[\frac{\left(N_{0.88}\times A_{2.01,\ FA}/N_{2.01}\times A_{0.88,\ FA}\right) - \left(N_{0.88}\times A_{2.01,\ EFA}/N_{2.01}\times A_{0.88,\ EFA}\right)}{N_{0.88}\times A_{2.01,\ FA}/N_{2.01}\times A_{0.88,\ FA}}\right] \quad (1)$$

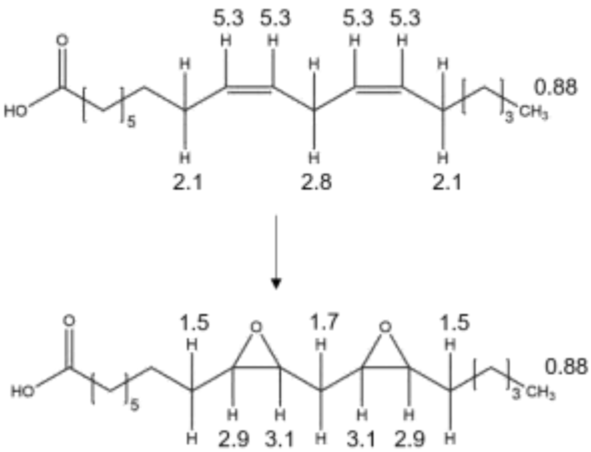


Fig 2. The assignments of the chemical shifts of important protons for Jatropha fatty acid and epoxidized Jatropha fatty acid

X	=	Conversion of double bonds
$A_{2.01,\ FA}$	=	Intensity at 2.01 ppm of Jatropha fatty acid (FA) spectrum
$A_{2.01,\ EFA}$	=	Intensity at 2.01 ppm of epoxidized Jatropha fatty acid (EFA) spectrum
$A_{0.88,\ FA}$	=	Intensity of internal standard in the Jatropha fatty acid spectrum
$A_{0.88,\ EFA}$	=	Intensity of internal standard in epoxidized Jatropha fatty acid spectrum
$N_{0.88}$	=	Amounts of protons of the internal standard ($N_{0.88} = 3$)
$N_{2.01}$	=	Amounts of protons of the signal at 2.01 ppm ($N_{2.01} = 4$)

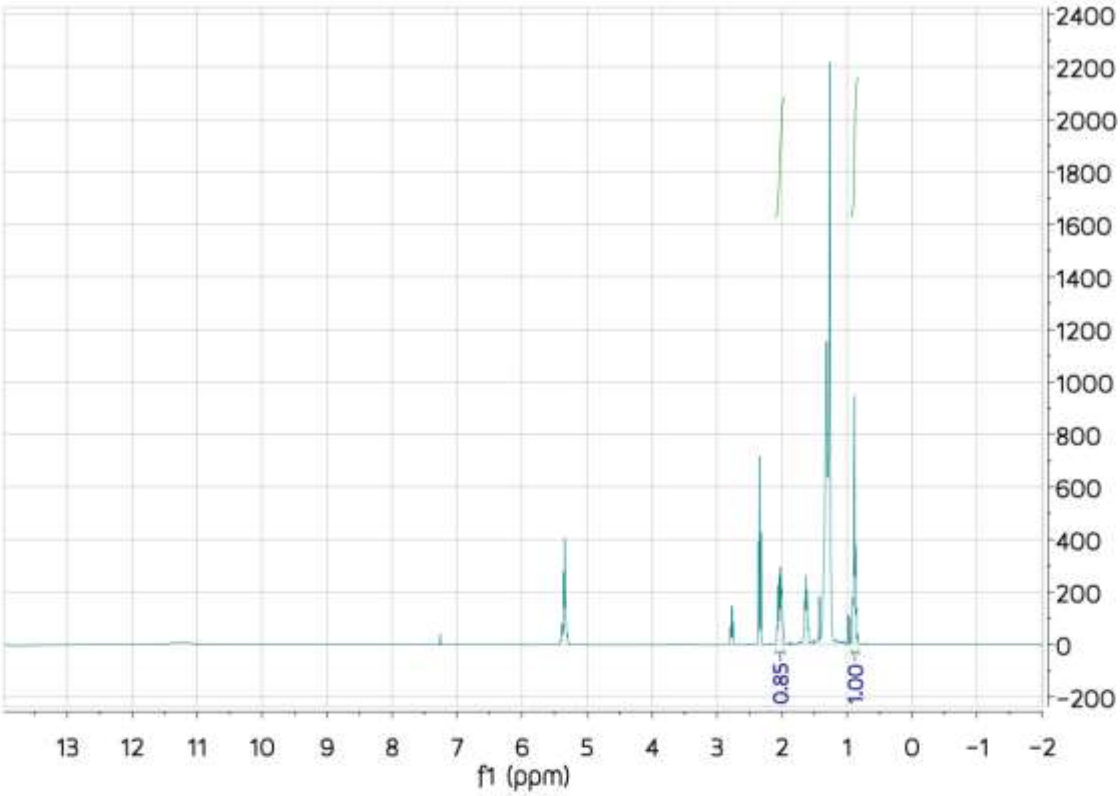


Fig 3. [1]H-NMR spectrum for Jatropha fatty acid

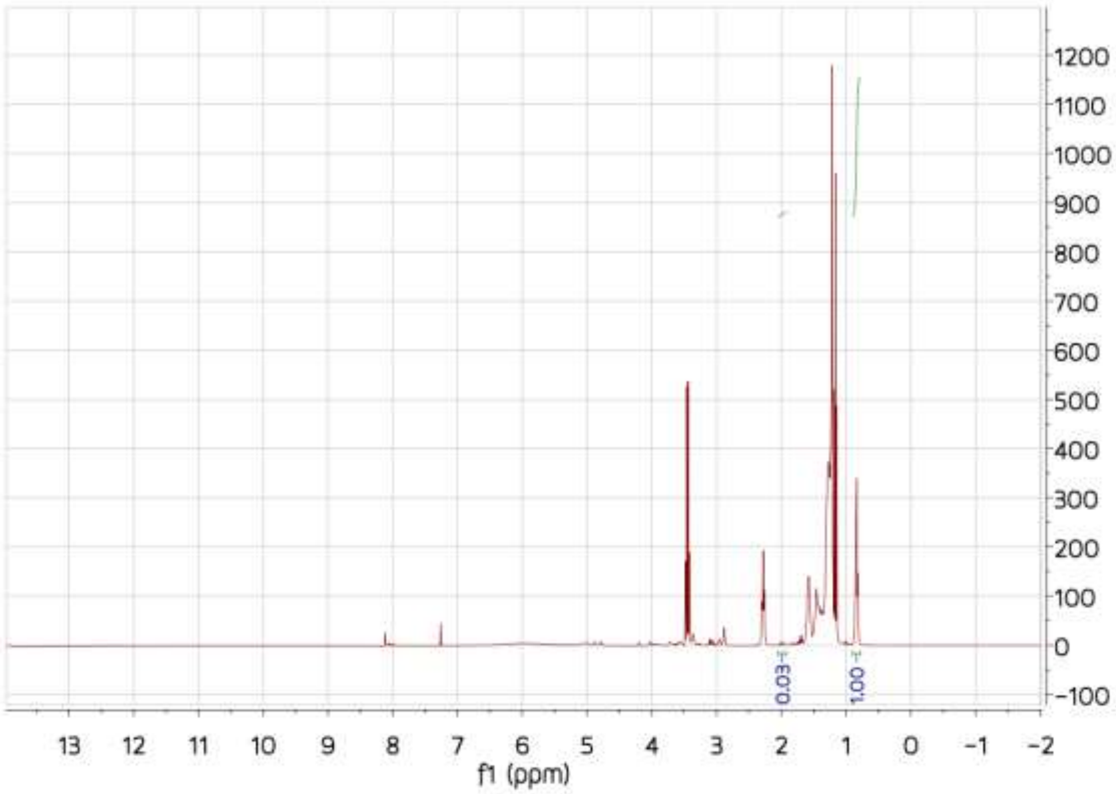


Fig 4. [1]H-NMR spectrum for epoxidized Jatropha fatty acid

The third and fourth step of modification were ring-opening reaction of epoxidation Jatropha fatty acid and esterification using Palm fatty acid distillate (PFAD) and 2-ethylhexanol as a precursor in sequence. The viscosity and viscosity index of hydroxy acyl derivative of fatty acid and hydroxy acyl derivative of fatty acid 2-ethylhexyl ester were calculated using ASTM methods D 445-97 and and ASTM D 2270-93, respectively. In addition, Oxidation stability was analyzed by Biodiesel Rancimat instrument at 110^{o} C. Table 3 showed the viscosity, viscosity index and oxidation stability of prepared products.

The results showed that removal of the unstable double bonds from Jatropha fatty acid result in an improvement of oxidation stability as shown in Table 3. Oxidation stability of Jatropha fatty acid (1) could be increased from 10.8 min to 46.2 min after epoxidation. On the other hand, oxidation stability of hydroxy acyl derivative of fatty acid decreased from 46.2 min to 18.0 min due to high unsaturation of PFAD (48.83% as shown in Table 2) used as a precursor in third step and oxidation stability of hydroxy acyl derivative of fatty acid 2-ethylhexyl ester was increased from 18.0 min to 25.7 min after esterification due to carboxyl group of hydroxy acyl derivative of fatty acid had a lower thermal and chemical stability than ester group of hydroxy acyl derivative of fatty acid 2-ethylhexyl ester. Moreover, increasing the molecular weight and changing the molecular structure resulted in an increased viscosity and viscosity index of products. Furthermore, hydroxy acyl derivative of fatty acid 2-ethylhexyl ester showed viscosity and viscosity index suitable for ISO VG 22 application.

Table 3 The viscosity, viscosity index and oxidation stability of Jatropha fatty acid (JFA), epoxidized Jatropha fatty acid (EJFA), hydroxy acyl derivative of fatty acid (HADFA) and hydroxy acyl derivative of fatty acid 2-ethylhexyl ester (HADFAEHE)

Products	Viscosity at 40◦C (cSt.)	Viscosity at 100◦C (cSt.)	Viscosity index	Oxidation stability at 110^{o} C (min)
JFA	-	-	-	10.8
EJFA	-	-	-	46.2
HADFA	19.64	5.07	177.52	18.0
HADFAEHE	23.70	14.52	186.49	25.7
ISO VG 22	19.8-24.2	>4.1	>100	-

Conclusion

Based on the results obtained, an increase the chain length of synthesized ester also had a positive influence on the tribological properties of the molecules. And, removal of the unstable double bonds from fatty acid, increased molecular weight and modify the molecular structure of Jatropha oil result in an improve lubricity properties of the synthesized esters. In addition, the result exhibited that these derivatives had significant potential to be used as bio-lubricant base stocks.

Acknowledgement

The authors would like to thank Department of Chemical Engineering from Kasetsart University, The graduate school from Kasetsart University and Center of Excellence on Petrochemical and Materials Technology (PETROMAT) for the financial support. KU-Biodiesel Project, Patum Vegetable Oil Co., Ltd. and Center of Excellence for Jatropha (COE) are gratefully acknowledged for supporting the raw material and equipment.

References

Adhvaryu, A., Liu, Z. and S.Z. Erhan. 2005. Synthesis of Novel Alkoxylated Triacylglycerols and Their Lubricant Base Oil Properties. Industrial Crops and Products. 21: 113-119.

Bart, J.C.J., E. Gucciardi and S. Cavallaro. 2013. Biolubricants. Woodhead Publishing, UK.

Chan, C.H., S.W. Tang, N.K. Mohd, W.H. Lim and S.K. Yeong. 2018. Tribological behavior of biolubricant base stocks and additives. Renewable and Sustainable Energy Reviews. 93: 145-157.

Fox, N.J. and G.W. Stachowiak. 2007. Vegetable oil-based lubricants - a review of oxidation. Tribology International. 40:1035–1046.

Hong, L.K., R.M. Yusop, N. Salih and J. Salimon. 2015. Optimization of the in-situ epoxidation of linoleic acid of Jatropha curcas oil with performic acid. The Malaysian Journal of Analytical Sciences. 19: 144-154.

Hwang, H., and S.Z. Erhan. 2001. Modification of Epoxidized Soyabean Oil for lubricant Formulations with improved Oxidized Stability and Low Pour Point. Journal of The American Oil Chemists Society. 78: 1179-1184.

Jayadas, N.H. and P.K. Nair. 2006. Coconut oil as base oil for industrial lubricants-evaluation and modification of thermal, oxidative and low temperature properties. Tribology International. 39: 873-878.

Madanhire, I. and C. Mbohwa. 2016. Mitigating Environmental Impact of Petroleum Lubricants. Springer International Publishing, Switzerland.

McNutt, J. and Q.S. He. 2016. Development of biolubricants from vegetable oils via chemical modification. Journal of Industrial and Engineering Chemistry. 36: 1-12.

Salih, N., J. Salimon, E. Yousif and B.M. Abdullah. 2013. Biolubricant basestocks from chemically modified plant oils: ricinoleic acid based-tetraesters. Chemistry Central Journal. 7: 128.

Salimon, J., B. Mudhaffar and N. Salih. 2011. Hydrolysis optimization and characterization study of preparing fatty acids from Jatropha curcas seed oil. Chemistry Central Journal. 5: 67.

Salimon, J., N. Salih and E. Youfit. 2012. Biolubricant basestocks from chemically modified ricinoleic acid. Journal of King Saud University – Science. 24: 11-17.

The Relationship between Prices of Crude Oil and Gold

Wiranya Sutthikun and Kongkiat Sahayrak

*Faculty of Business Administration and Management, Ubon Ratchatani Rajabhat University

E-Mail: Wiranya.s@ubru.ac.th

Abstract

The paper analyses the relation between the prices crude oil and gold prices. The purpose of the paper is to establish the determinants, co-movement, and the character existing between the two prices. The paper looks through the crude oil and gold prices traded in different regions for the past twenty years. The relation existing between the price levels of gold and oil is analyzed using the gold to oil ratio, which is calculated as part of the price of gold to the price level of crude oil about time. Further, a correlation analysis test is adopted which establishes the positive strength of the gold and crude oil price relationship.

Keywords : Price relationship, crude oil, gold

Introduction

Interconnectivity trend is prevalent in the commodity market with crude oil and gold playing a crucial role. Gold is the oldest and precious metal that is known to man, which is valued as a global currency, object of beauty, investment, and a commodity. Besides, crude oil is considered the mother of all other commodities because it is essential in the manufacture of extensive materials. The interconnection between the two commodities started in 1933, as the crude oil producers from the Middle East were demanding gold in exchange for crude oil (Fratzscher, Schneider, & Robays, 2014). Both crude oil and gold are quoted in US dollars. A quantitative and theoretical analysis present an overview of the relation between the prices of crude oil and gold. The primary characteristics of the products in diverse scenarios alongside the factors influencing the products in the markets are presented in the paper. The correlation analysis test and the gold to oil ratio are employed to establish the relation between the prices of crude oil and gold prices.

Overview of Crude Oil and Gold Trade

Gold is the oldest international currency in the world, which has been an essential element of the international monetary reserve. India is the world largest market for jewelry and a major driver of global demand for gold. Households in India possess more gold than other households across the globe. Two-thirds of demanding gold is obtained from rural areas in which jewelry is considered a traditional store wealth among people with limited access to the systems of conventional banking. In light of this, Sovereign Gold Bonds Scheme was approved alongside Gold Monetization Scheme in the Union (Sumner, Johnson, & Soenen, 2010). Schemes were created to ensure the monetization of the gold that was idle in the economy as well as satisfy the increased demand for gold without the need for retaining the physical gold. The decision of the government to launch the schemes is useful for translating the gold savings into economic investments alongside making the precious metal a crucial part of the financial system.

Throughout the history, gold has been a major monetary standard. States and empires have been rising and falling with a single fiat currency that has been in a position to sponsor governments. Gold was the standard by which currencies obtained a judgment, as it was considered the only real money (Bill Haynes, 2015). Based on its high value, gold is highly sought after internationally. However, gold is scarce in the nature that makes its supply challenging.

Crude oil is a mixture of various hydrocarbons, which are found in upper parts of the crust. Typically, crude oil is referred to as the father of nations as it is essential for making diverse commodities. Crude is essential for producing fuel used for trains, airplanes, buses, and cars. Besides, it is utilized for making products such as plastic for toys, asphalt for roads, bottles, and lubricants. Presently, India is among the leading importers of crude oil alongside China and the United States. For instance, in 2015, oil imports were valued at the price of US $7357.47 (Wang, Wang, & Huang, 2010). Almost every product consumed across the globe is transported using oil-powered aeroplanes, ships, trucks, and trains. Thus, in the absence of oil, most of the commodities utilized internationally would be unavailable, making it difficult to sustain global trade.

Characteristics of Crude Oil and Gold

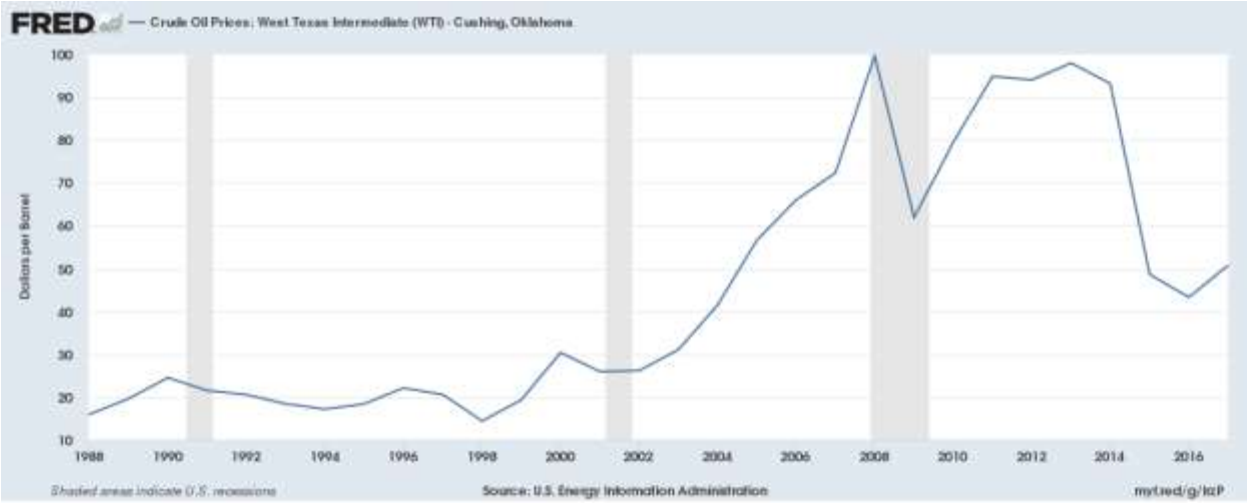
Compared to other assets the evaluation of gold is very difficult. Gold is similar to currencies such as Euro and US dollar because it is portable, durable, widely accepted and uniform across the globe. Different from other currencies, the support for gold is realized from companies and infrastructure. Moreover, gold is considered to be similar to maize or even oil because it is obtained from the ground and has different characteristics.

Figure 1: Gold prices in 1987 - 2017

Source: Federal Reserve Economic Data

In addition, different from the other commodities, the pricing level for gold normally fluctuates without being affected by levels of supply and demand. Over 10% of the world's gold is utilized by industries, especially in electronics based on its anticorrosive and conductivity. Apart from this, gold is used for jewelry and investments.

Figure 2: Oil prices in 1987 - 2017



Source: Federal Reserve Economic Data

There are various types of crude oil produced across the globe. These types vary based on their quality and their characteristics. The crude oil types primarily utilized are Brent and West Texas Intermediate. The Petroleum and crude oil are international commodities that make their prices dependent on the factors of supply and demand. The pricing level of crude oil is a vital factor that influences the pricing levels of all the petroleum products which the most important currency is USD, most oil trading conducted and through USD. There is an indirect correlation between dollar and oil prices. As a result, the costs of transportation increases which in return raises the costs of manufacturing as well as distribution. Thus, the final price level of the product is affected, that in its turn adds up to inflationary pressure. The forces of supply and demand influence the price levels of crude oil across the globe. The decision for the supply of crude oil lies in the hands of the OPEC nations, which makes the supply of oil limited. From figure 2 show the oil price collapse in 1988, oil prices has fallen since the end of November 1987 lower as $18 per barrel. Oxford Institute for Energy Studies (1998) said the reason for this fallen price fluctuation crisis is the over production in 1997 and early 1998 destroyed the balance of supply demand fundamentals. Also in 2002 there is apparent instability during the period of earthquake and hurricanes when the production capabilities are limited.

The Link between Gold and Oil Markets

The prices of gold and crude oil develop in a similar path. If the valuation of the US dollar drops, the price levels of gold remain intact all over the world but in the US market, more money is paid for gold purchased. Differently, if the same dollar falls, the price level of oil in the United States rises oddly, but it falls in other nations, based on the fact that crude oil trading's currency is the US dollar. Moreover, oil is utilized for excavating as well as refining gold; hence, increased prices on oil correspond to increased prices of gold (Narayan, Narayan, & Zheng, 2010). Besides, the recent increase in oil prices has made it impossible for the movement of crude oil and gold to be in tandem.

Further, when the participants and the hedgers make demands using Euros, then the fall becomes pronounced as the impact of price on the valuable metal increases. This can be linked to the situation of excess cash flow being placed on limited goods. Other than, the lag between the price of gold and the movement of the dollar in the short run does not affect the relation between the two in the long run. In the case where the price of oil increases and there is a diversification in demand for the dollar, then more dollar on oil is used on gold.

Nevertheless, the gold to oil ratio is utilized for expressing the relationship between the two commodities that are crucial for forming the foundation of the entire economy. The gold to oil ratio is considered valuable as it shows the expression of the complicated relationship between crucial global commodities (Mollick & Assefa, 2013). The ratio makes it possible to notice when the prices of gold or oil are high and bring in the possibility of reversion. The prices of gold and crude oil fall and rise depending on each other as the purchases of oil were performed using gold. Besides, in the current market, the revenue accumulated from oil is used to make investments in gold. On that account, as the prices of oil increase, more revenue to be invested in gold is obtained. High prices attached to crude oil increase inflation pressure, which is essential for boosting the appeal for gold. This indicates that crude oil and gold prices obtaining a positive correlation.

Studies on the Relation between the prices of Crude Oil and Gold

Caballero, Farhi, and Gourinchas (2008) utilized the GARCH and the ARCH modes to determine the relation between gold and oil markets using the channel of export revenue. The results of their study revealed that when the price levels of oil increased the revenue resulting from the exportation of oil increased which directly affected the price levels of gold. Further et al., (2008) concluded that the price level of crude oil variations alongside the timing of making supplies vary based on the premium of gold in its future prices, which were seen to depend on its conditional variance on spot prices. The GARCH model presents a context in real life and focuses on predicting the rates and prices of various financial instruments. Moreover, it defines the conditional variance of the relationship between gold and crude oil prices as being a linear function. Lastly, GARCH and ARCH models soften the linear restriction that may be imposed on the dynamics of conditional variance.

Kang and Yoon (2013) determined the long run relation existing between oil and gold future and spot markets using different periods and the structural break cointegration test. They outlined that the rise in the prices of oil influences an increase in the rate of inflation, resulting in increased prices of gold. This means that investors utilize the gold market as the hedger of inflation, using the oil market to make predictions on the prices of gold in the market. Additionally, Masih, Peters, and De Mello (2011) established a cointegration relation between the gold market and the crude oil market. This means that the volatility of the crude oil prices is higher than that of gold, which brings about a long-term relation in its equilibrium.

According to Chkili, Hammoudeh, and Nguyen (2014), variations in political conflicts and changes in the prices of crude oil are major determinants of the price rate assigned to gold. A bidirectional causality was identified as the long-term relation between oil and gold. In the presence of some common factors, Fratzscher (2009) indicates that future prices of all the energy commodities brings about the correlation between the prices of oil and gold. Gaur and Bansal (2010) analyzed the causality between oil and gold prices and established that a consistency in the trends of gold and oil prices as they adopted a positive correlation. The dynamics of the price of oil are linearly Granger leading to the volatility of the gold prices. Other than that, Le and Chang (2012) analyzed the gold-oil dependence structure utilizing a copula approach between 2000 and 2011 after which they established an important and interdependent relation between gold and crude oil.

Data Sourcing and Empirical Findings

Correlation analysis

Correlation analysis represents a statistical tool, which is utilized to present the description of the degree to which one of the variables is related to other linearly (1997 - 2017).

We using equation of correlation coefficient

$$\mathbf{r} = \frac{\sum_i (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_i (x_i - \bar{x})^2}\sqrt{\sum_i (y_i - \bar{y})^2}}$$

	Price of Crude Oil WTI in USD	Price of Gold in USD
Price of Crude Oil	0.84	1
Price of Gold	1	0.84

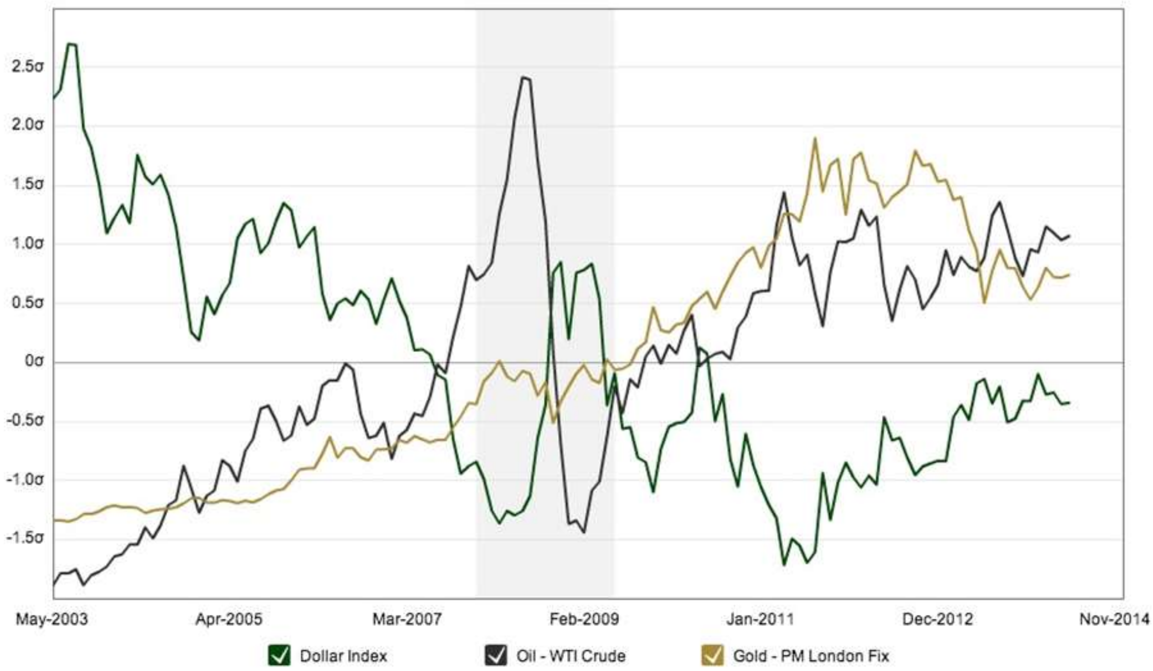
Source: author's calculations

It is evident from the table that the degree of correlation is 0.8478 on positive. Hence, the statement that both crude oil and gold shows a linear relationship. This relationship can be analyzed utilizing the Gold to Oil ratio.

Gold to Oil Ratio

As indicated above, the gold to oil ratio represents the barrels of crude oil required to purchase around ten grams of gold. If the ratio is rising, it implies that more of the oil barrels are required to purchase ten grams of gold (Gilmore, McManus, & Sharma, 2009). In the case where the ratio is decreasing, in a relative sense, it implies that oil is becoming more expensive to gold. By coming up with a measure for the price level of oil against the price level of gold, a valuable perspective regarding the actual values of gold and crude oil against the currency in which they are priced can be used. The gold to oil ratio is calculated by dividing the price of ten grams of gold by the price level of crude oil in a single barrel. This ratio measures "how many barrels of oil one can buy with an ounce of gold" and is calculated as:

Gold-Oil Ratio = Price of Gold (per oz.) / Price of Crude Oil (per barrel)



The chart indicates sharp falls and rises of oil prices that can be seen in black line, which are accompanied by significant changes in the price of gold in gold line. The interaction of two commodity prices shows that there is an inverse relation between the prices of gold and crude oil and the green line represents the US dollar.

Oil prices are influenced by stock markets, trade, and gold weighted USD exchange rates. Future prices of oil influence the prices of oil. On the other hand, the prices of gold are based on the variations in oil, stock markets, and the US dollar and depend on the default premium and the United States oil imports. The exchange rate of the US dollar is highly affected by the stock market, gold, and oil prices.

Nevertheless, with the financial process in the commodity markets, gold, crude oil, and stock prices, the US dollar adopts diverse properties (Ewing & Malik, 2013). A positive correlation is realized in their relationship based on the international business cycle. Thus, the price dynamics of gold and crude oil are vital indicators of the expectations in the market on the state of the world investments and the economy.

Conclusion

Based on the analysis conducted, the general thought is that the price levels of crude oil and gold have a correlation that is positive. The inter-relationship between the two is caused by the valuation of their levels in US dollars. Crude oil and gold are quoted in dollars across the global markets. In the case where Dollars should weaken against currencies such as the Rupee, then all imported items such as gold and oil end up costing more in Dollars, which indicates the inter-relation between the prices of crude oil and those of gold.

Regarding the return analysis, the conclusion is that the current return influences the previous return of gold and crude oil. Investors are supposed to be keen and make analysis of the return and previous prices imposed on gold and crude oil for them to be in a position to determine the strategies to adopt while running investments on the future market of the two commodities. Nevertheless, there are some gaps in the relationship between the return prices of oil and that of gold. However, the volatility of the analysis of the price return indicates that the volatility of the gold price return influences the volatility of crude oil price returns. With its establishment, investors are in a position to monitor the variations of the price return of gold through being keen on the volatility of the price return of crude oil.

References

Bill Haynes (2015). Retrieved from https://www.cmi-gold-silver.com/why-gold-is-real-money/

Caballero, R. J., Farhi, E., & Gourinchas, P. O. (2008). *Financial crash, commodity prices and global imbalances* (No. w14521). National Bureau of Economic Research.

Chkili, W., Hammoudeh, S., & Nguyen, D. K. (2014). Volatility forecasting and risk management for commodity markets in the presence of asymmetry and long memory. *Energy Economics*, *41*, 1-18.

De Schryder, S., & Peersman, G. (2013). The US dollar exchange rate and the demand for oil.

Ewing, B. T., & Malik, F. (2013). Volatility transmission between gold and oil futures under structural breaks. *International Review of Economics & Finance*, *25*, 113-121.

Fratzscher, M. (2009). What explains global exchange rate movements during the financial crisis? *Journal of International Money and Finance,* 28(8), 1390-1407.

Fratzscher, M., Schneider, D., & Van Robays, I. (2014). Oil prices, exchange rates and asset prices.

Gaur, A., & Bansal, M. (2010). A comparative study of gold price movements in Indian and global markets. *Indian Journal of Finance*, *4*(2), 32-37.

Gilmore, C. G., McManus, G. M., Sharma, R., & Tezel, A. (2009). The dynamics of gold prices, gold mining stock prices and stock market prices comovements. *Research in Applied Economics*, *1*(1).

Kang, S. H., & Yoon, S. M. (2013). Revisited return and volatility spillover effect in Korea. *Korea and the World Economy*, *14*(1), 121-145.

Le, T. H., & Chang, Y. (2012). Oil price shocks and gold returns. *International Economics*, *131*, 71-103.

Masih, R., Peters, S., & De Mello, L. (2011). Oil price volatility and stock price fluctuations in an emerging market: evidence from South Korea. *Energy Economics*, *33*(5), 975-986.

Mollick, A. V., & Assefa, T. A. (2013). US stock returns and oil prices: The tale from daily data and the 2008–2009 financial crisis. *Energy Economics*, *36*, 1-18.

Narayan, P. K., Narayan, S., & Zheng, X. (2010). Gold and oil futures markets: Are markets efficient?. *Applied energy*, *87*(10), 3299-3303.

Oxford Institute for Energy Studies (1998). Retrieved from https://www.oxfordenergy.org/wpcm TheOilPriceCrisisof1998-RMabro-1998.pdf

Sumner, S., Johnson, R., & Soenen, L. (2011). Spillover effects among gold, stocks, and bonds.

Wang, M. L., Wang, C. P., & Huang, T. Y. (2010). Relationships among oil price, gold price, exchange rate and international stock markets. *International Research Journal of Finance and Economics*, *47*, 80-89.