

THERMAL CATALYTIC DECARBOXYLATION OF MG-ZN BASIC SOAP TO PRODUCE DROP-IN FUELS IN JET FUEL BOILING RANGES.

Godlief F. Neonufa^{ab*}, Tatang H. Soerawidjaja^a and Tirto Prakoso^a

^a Department of Chemical Engineering
Institut Teknologi Bandung, Bandung 40132 Indonesia

^b Department of Agriculture Product Technology
Universitas Kristen Artha Wacana, Kupang 85000 Indonesia

Author(s) e-mail: godlief17@students.itb.ac.id

Abstract

Deoxygenation of Fatty acid or their derivatives is a method for producing renewable hydrocarbon fuels such as jet biofuel, green diesel and biogasoline. In the present commercial method, deoxygenation is directly applied to vegetable oils through liquid phase hydrotreatment. This method is expensive because it requires the use of problematic sulfided catalysts and high pressure of hydrogen and requires severe operating conditions. The objective of this study was to produce alkane biohydrocarbons, particularly jet fuel that can be considered to be drop-in replacements for petroleum-based jet fuel components, by catalytic thermal decarboxylation of Mg-Zn basic soap. Specifically, this study investigated the decarboxylation of the basic soap at mild operating conditions without external supply of hydrogen. The Mg-Zn basic soap (9/1 mol ratio of Mg/Zn) was derived from fatty acid methyl esters C₁₂/C₁₆ of palm kernel oil and decarboxylated for 3 hours at atmospheric pressure and temperatures between 250 to 350 °C. The basic soap effectively decarboxylated yielding a jet fuel-type biohydrocarbons, with a liquid product yield of 42,94%-weight. The resulting hydrocarbon product is a complex mixture consisting of normal paraffins in the range of carbon chain length C₈ - C₂₀, iso- and cyclo-paraffins and the various olefin products.

Keywords: deoxygenation, decarboxylation, basic soap, hydrocarbon, drop-in fuel, jet biofuel.

INTRODUCTION

Interest in renewable fuels has been encouraged in recent years by a number of environmental, economic and geopolitical considerations, including global warming, dwindling petroleum deposits, rising crude oil prices and a desire for energy independence. Against this background, biofuels have been proposed as a renewable, carbon-neutral alternative to fossil fuels. Renewable hydrocarbon biofuels (also called biohydrocarbons and/or drop-in biofuels) are fuels produced from biomass sources through a variety of biological and thermochemical processes. Biomass such as oils and fats are the feedstock candidates that very potential and promises to produce renewable fuels (Kubickova et al. 2005, 197-200; Ma'ki-Arvela et al. 2007,30-41). Approximately 201.1 million tons of oils and fats were produced worldwide in 2014, from animal and vegetable feedstocks (FAO 2014).

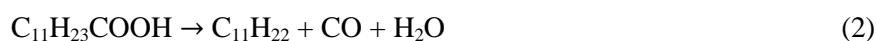
The production of renewable fuel is an emerging option to increase the availability of liquid fuels and achieve the goal set by the Indonesia government of replacing 20% of the nation's petroleum consumption with renewable alternatives by 2020 (Fu et al. 2011, 227 – 231; Soerawidjaja 2013). Drop-in biofuels are liquid transportation fuels made from oils and fats. These fuels are similar to petroleum gasoline, diesel, or jet fuel in chemical makeup and are therefore considered fully

infrastructure-compatible fuels. They can be used in vehicles without engine modifications and can utilize existing petroleum distribution systems (U.S. Department of Energy 2016). Jet biofuel meets or exceeds the most rigorous jet fuel standards for performance. For example, blending the jet biofuel in a 50/50 ratio with petroleum-based jet fuel gives offers significant advantages over petroleum jet fuel, such as can reduce greenhouse gas emission by 65-85% compared with petroleum-based fuels. Moreover, has shown higher energy density in flight, which allows aircraft to fly farther on less fuel. Furthermore, meets or exceeds critical jet fuel specifications, such as: flash point, freeze point, stability and heat of combustion (Honeywell UOP 2016). Fatty acids and their derivatives such as fatty acid methyl esters (FAME) C₁₂/C₁₆ of palm kernel oil can be converted to renewable and carbon-neutral fuel-like hydrocarbons (e.g. jet biofuels) that are entirely fungible with fossil fuels by deoxygenation methods. This method can be conducted via decarboxylation, decarbonylation and hydrodeoxygenation pathways, as illustrated below for lauric acid.

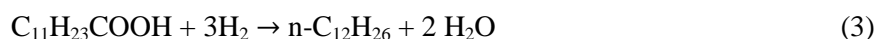
Decarboxylation yields CO₂ and n-undecane:



Decarbonylation yields CO, water and undecenes:



Hydrodeoxygenation yields H₂O and n-dodecane:



In the present commercial method, hydrodeoxygenation (-H₂O) via hydrotreatment is directly applied to vegetable oils through liquid phase hydrotreatment. This method is expensive because it requires the use of problematic sulfided catalysts and high pressure of hydrogen and requires severe operating conditions.

In view of this, an alternative has been sought in the deoxygenations of triglycerides and fatty acids or their derivatives via basic soap decarboxylation (-CO₂). The literatures report that soaps made from vegetable oils or fats can be processed into products that are rich in hydrocarbons by pyrolysis reaction with high yields and temperatures not so high as expected (Demirbas 2006, 619-626). Decomposition of the alkali and alkaline earth metals soaps of the higher fatty acids generally gives better yields of hydrocarbon than that of obtained by decomposition of the corresponding fatty acids or fats (Ralston 1948). Chang and Wan have been studied the formation of hydrocarbons which correspond to its oil fraction. The products are obtained from catalytic and thermal cracking of vegetable oils and soaps. Pyrolysis calcium soaps derived from rapeseed oil, peanut oil and Tung oil (Chang and Wan 1947) was conducted and appears to be effective to produce hydrocarbons that have the physical-chemical properties similar to the specifications of fossil oil fractions. Basic soap decarboxylation as illustrated below (also with lauric acid), has not been studied intensively to be developed on an industrial scale.



When compared with hydrodeoxygenation via hydrotreating and hydro-decarboxylation of the fatty acids or their derivatives, basic soap decarboxylation permit the use of simpler catalysts and require less hydrogen, which makes deoxygenation via basic soap decarboxylation appealing from an economic standpoint (Santillan-Jimenez and Crocker 2012, 1041-1050). Therefore, basic soaps decarboxylation has emerged as a route that very promising to developed becomes the basis of a commercial decarboxylation process.

The objective of this study was to produce alkane bio-hydrocarbons (especially in the chain length ranges of jet biofuel) that can be considered to be drop-in replacements for petroleum-based jet fuels components, by catalytic thermal decarboxylation of Mg-Zn basic soap. In particular, this study investigated the decarboxylation of the basic soap at mild operating conditions without external supply of hydrogen.

Experimental

Magnesium acetate tetrahydrate [Mg(OOC₂H₅)₂·4H₂O] and zinc acetate dihydrate [Zn(OOC₂H₅)₂·2H₂O] was supplied by Merck (analytical grade), were used to make the soap. The fatty acid methyl esters (FAME) C₁₂/C₁₆ of palm kernel oil obtained from PT. Ecogreen, Batam. The Mg-Zn basic soap were obtained metathesis process. The process started by mixing FAME and hot ethanol. Then, stirred the mixture with an aqueous solution of sodium hydroxide at 20% (w/w) until it has reached a firm consistency. While continually stirring, to this mixture is then added slowly a solution of magnesium acetate tetrahydrate and zinc acetate dihydrate in distilled water. The resulting basic soaps were filtered, washed (by hot water) and dried for use in subsequent experiments. Saponification reactions were performed in a glass batch reactors.

Decarboxylation reaction were also performed in a 100 ml glass batch reactor at atmospheric pressure with a water-cooled condenser. Heat was supplied by a high temperature heating mantle and both liquid (the melted soap) and vapor temperatures were measured with thermocouple. Mg-Zn basic soap from FAME C₁₂/C₁₆ of palm kernel oil as a reactant model compound and the reactions were performed without the aid of other catalysts. Decarboxylation proceeded at temperatures between 250 to 350°C for 3 hours.

In a typical batch experiment, a number of basic soaps carefully weighed were placed into the reactor. After that, the reactor was flushed with nitrogen in order to remove the remaining oxygen. Then, the reactor was heated to 350°C and maintained for 3 hours at that temperature. The liquid products were collected in a beaker.

The liquid reaction products were analyzed by gas chromatograph (Shimadzu 2010) equipped with a capillary column (rtx-1) with dimensions of 30 m x 0.25 mm x 0.25 µm and flame ionization detector. One microliter of sample was injected into the GC with a split ratio 1:50 and the carrier gas (helium) flow rate was 42.9 ml/min. The injector and detector temperature were 340°C and 340°C, respectively. The following chromatographic temperature program was used for analysis: 40°C (at first) – 300°C (5°C/min) – 340°C (1°C/min, constant 45 min). A number of chemical standards were purchased enabling product identification and calibration. Determination of the freezing point have been tested with ASTM D-2500 procedures.

RESULTS AND DISCUSSION

This section presents information about the product observed from the decarboxylation reactions of Mg-Zn basic soap of FAME C₁₂/C₁₆ of palm kernel oils.

Product Yield from Decarboxylation

Table 1 shows various products that arises form Mg-Zn basic soap decarboxylation to 350°C for 3 hours and at atmospheric pressure.

Table 1. The results of Mg-Zn basic soap decarboxylation.

<i>Types of product</i>	<i>Yields [%-wt]</i>
<i>liquid bio-hydrocarbons</i>	<i>42.94</i>
<i>water</i>	<i>4.57</i>
<i>solid residues</i>	<i>31.70</i>
<i>others (include the gas)</i>	<i>20.79</i>

These result showing that liquid bio-hydrocarbon yields to 42.94 %-weight, were produced via decarboxylation of Mg-Zn basic soap from FAME C₁₂/C₁₆ of palm kernel oils. It is prove that liquid bio-hydrocarbons could be synthesized from basic soap as a reactants. It also shows that the combination of Mg-Zn metals have good catalytic activity for converting the reactants (Mg-Zn basic soap from FAME C₁₂/C₁₆ of palm kernel oils) into hydrocarbons via decarboxylation reaction to 350°C

for 3 hours. This result show that the renewable hydrocarbon synthesis via basic soap decarboxylation not depend on the presence of Pt and Pd (precious metals) catalysts, and high pressure operation, as reported by previous researchers (Fu et al. 2010, 311-317; Snare et al. 2008, 933-945).

Physicochemical Properties of Liquid Bio-hydrocarbon Product

Table 2 shows some selected physicochemical properties of liquid bio-hydrocarbons product of Mg-Zn basic soap from FAME C₁₂/C₁₆ of palm kernel oils to 350°C for 3 hours.

Table 2. Physicochemical Properties of Liquid Biohydrocarbon.

<i>Components</i>	<i>Value</i>
<i>Acid value (mg KOH/gr sample)</i>	0.5
<i>Freezing point (°C)</i>	< 15
<i>Ketones/aldehydes group (-/+)</i>	-

Acid value in liquid bio-hydrocarbon product is very small (0.5 mg KOH / g sample). It is shows that all about of the free fatty acid (from FAME C₁₂/C₁₆ of palm kernel oils) has been converted into basic soap and subsequent to converted by decarboxylation reaction into bio-hydrocarbon. For the freezing point, Table 2 shows that liquid bio-hydrocarbon product were obtained of Mg-Zn basic soap just not dominated by n-undecane (their freezing point is 21,0°C) as which are expected from FAME C₁₂/C₁₆ of palm kernel oils (C₁₂ predominantly fatty acids), but also consisted of mixture of bio-hydrocarbon with various of carbon chain length ranges, particularly short chain molecule bio-hydrocarbons that has a lower freezing point.

Distribution of Liquid Bio-hydrocarbon Products.

GC-FID chromatograms patterns associated to distribution of liquid bio-hydrocarbon fraction were obtained from decarboxylation of Mg-Zn basic soap from FAME C₁₂/C₁₆ of palm kernel oils to 350°C for 3 hours, shown in Figure 1.

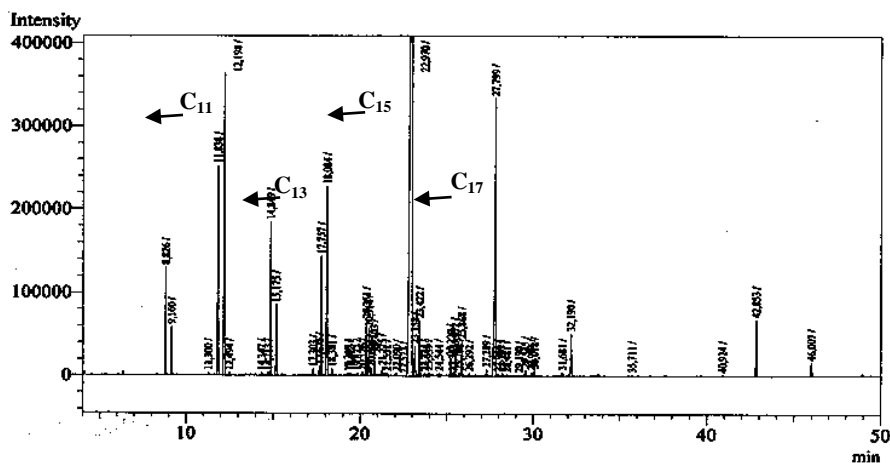


Figure 1. GC-FID chromatograms patterns for liquid bio-hydrocarbon fractions.

Figure 1 shows that decarboxylation of Mg-Zn basic soap was produced liquid bio-hydrocarbons in very diverse boiling range that is C₈ to C₂₀. The normal pentadecane (n-C₁₅) observed as the dominant component in the liquid bio-hydrocarbon product at retention time around 28 minutes, followed by normal undecane (n-C₁₁) that observed at retention time around 12 minutes. When the basic soap decarboxylation reaction has perfectly occur, it should produces higher normal undecane (n-C₁₁) component, because the FAME C₁₂/C₁₆ of palm kernel oil have more the fatty acids with C₁₂ (lauric acids) contain to 66.57%-wt (also 23.56%-wt of myristic acid/C₁₄ and 7.34%-wt of palmitic

acid/C₁₆). However, also observed the bio-hydrocarbon with C₈ to C₁₀ fraction at a retention time bellow 12 minutes with significant intensity. Moreover, also found the long-chain biohydrocarbon with C₁₇ (n-heptadecane) fraction, while in the FAME there is no fatty acid with C₁₈ (stearic acid) component. It is indicate that, under the conditions of the experiment, just not decarboxylation reaction proceeded, but also may have been a catalytic thermal cracking and/or polymerization raction of liquid bio-hydrocarbon were obtained, into smaller and/or higher molecules that are more according to bio-gasoline and green diesel.

The result of GC-FID chromatogram analysis related to the distribution of the liquid bio-hydrocarbon fraction were obtained from Mg-Zn basic soap decarboxylation are summarized in Table 3.

Table 3. The results of GC-FID chromatogram analysis of liquid bio-hydrocarbons.

<i>Bio-hydrocarbon compounds</i>	<i>formulas</i>	<i>Product Yields (%-mole)</i>
<i>n-octane</i>	<i>C₈H₁₈</i>	<i>1,533</i>
<i>1-octenes</i>	<i>C₈H₁₆</i>	<i>0,896</i>
<i>n-nonane</i>	<i>C₉H₂₀</i>	<i>3,534</i>
<i>1-nonenes</i>	<i>C₉H₁₈</i>	<i>2,286</i>
<i>n-decane</i>	<i>C₁₀H₂₂</i>	<i>4,386</i>
<i>1-decenes</i>	<i>C₁₀H₂₀</i>	<i>5,718</i>
<i>n-undecane</i>	<i>C₁₁H₂₄</i>	<i>11,437</i>
<i>1-undecenes</i>	<i>C₁₁H₂₂</i>	<i>5,111</i>
<i>n-dodecane</i>	<i>C₁₂H₂₆</i>	<i>2,259</i>
<i>1-dodecenes</i>	<i>C₁₂H₂₄</i>	<i>2,281</i>
<i>n-tridecane</i>	<i>C₁₃H₂₈</i>	<i>5,931</i>
<i>1-tridecenes</i>	<i>C₁₃H₂₆</i>	<i>1,971</i>
<i>n-tetradecane</i>	<i>C₁₄H₃₀</i>	<i>1,485</i>
<i>1-tetradecenes</i>	<i>C₁₄H₂₈</i>	<i>0,082</i>
<i>n-pentadecane</i>	<i>C₁₅H₃₂</i>	<i>29,720</i>
<i>n-heptadecane</i>	<i>C₁₇H₃₆</i>	<i>5,994</i>
<i>n-nonadecane</i>	<i>C₁₉H₄₀</i>	<i>0,939</i>
<i>Other paraffins</i>	<i>>C₁₉</i>	<i>0,798</i>
<i>i-paraffins</i>		<i>13,640</i>

Table 3 shows that, approximately 29.72 %-mole of n-pentadecane were obtained from decarboxylation of Mg-Zn basic soap of FAME C₁₂/C₁₆ of palm kernel oil. Whereas, n-undecane (C₁₁H₂₄) as most expected the major fraction, only obtained around 11.44%-wt. The rest fraction is dominated by higher and lower n-paraffin molecules, also olefin and iso-paraffin molecules.

The composition group of n-paraffin, olefins and iso-paraffin in the liquid bio-hydrocarbon were obtained from Mg-Zn basic soap decarboxylation of Mg-Zn basic soap of FAME C₁₂/C₁₆ of palm kernel oil, shown in Figure 2.

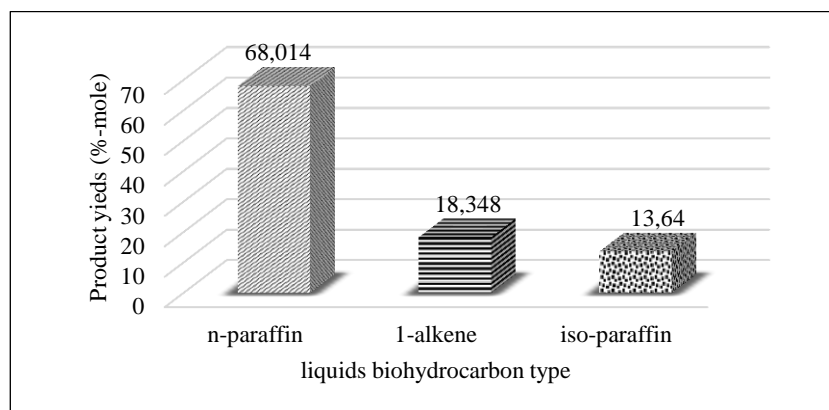


Figure 2. liquid bio-hydrocarbon types Mg-Zn basic soap decarboxylation.

Figure 2 shows that, approximately 81.7%-mole (that is n-paraffin + iso-paraffin) of liquid bio-hydrocarbon were obtained from Mg-Zn basic soap decarboxylation are paraffin molecules which there are expected in jet fuel. Their rest (around 18.3%-mole) are various 1-alkenes molecules. The presence of 1-alkene in significant amount shows that there has been a hydrogen consumption during the decarboxylation reaction by a specific element or residual oxygen in the reactor. In particular, Figure 3 shows the carbon chain length distribution of n-paraffin type in liquid bio-hydrocarbon was produced from Mg-Zn basic soap of FAME C₁₂/C₁₆ of palm kernel oil to 350°C for 3 hours.

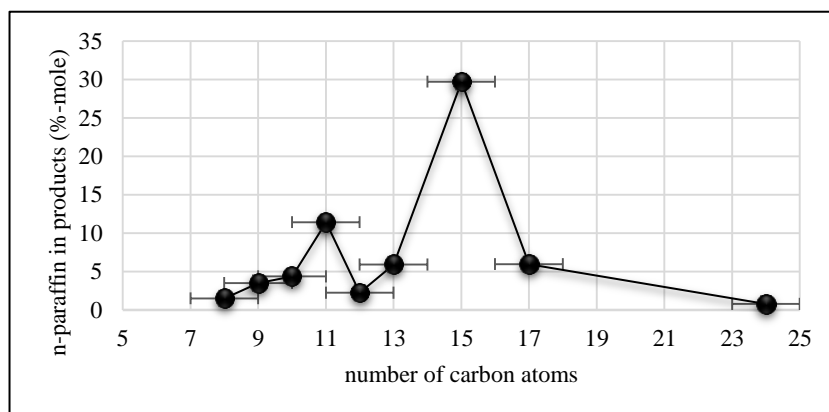


Figure 3. Distribution of liquid n-paraffin plot according to carbon chain length.

Figure 3 shows that bio-hydrocarbon with carbon chain length C₁₅ (n-pentadecane) most dominant (29.720 %-mole) in the liquid product of Mg-Zn basic soap decarboxylation to 350°C for 3 hours. The bio-hydrocarbon with further carbon chain length are C₁₁ (n-undecane, 11.437 %-mole), C₁₇ (n-heptadecane, 5.994%-mole) and other n-paraffin molecules that lower than C₁₅, respectively.

CONCLUSION

The drop-in fuels (liquid bio-hydrocarbon) in jet fuel boiling range, can be synthesized via basic soap decarboxylation, without the aid of hydrogen from the outside and the using not of commercial catalyst. The Mg-Zn basic soap (9/1 mol ratio of Mg/Zn) was derived from FAME C₁₂/C₁₆ of palm kernel oil and decarboxylated for 3 hours at atmospheric pressure and temperatures between 250 to 350°C, effectively yielding a jet fuel-type bio-hydrocarbons, with a liquid product yield of 42.94%-weight. The resulting hydrocarbon product is a complex mixture consisting of normal paraffins in the range of carbon chain length C₈ - C₂₀, iso-paraffins and the various olefin products.

Acknowledgement

This work is part of the doctoral research at Department of Chemical Engineering Institut Teknologi Bandung. I acknowledge Dr. Tatang H. Soerawidjaja and Dr. Tirto Prakoso for their constructive reviews of article and helpful discussion.

REFERENCES

- Chang, C.C. and Wan S.W. (1947). China's motor fuels from Tung oil. *Industrial and Engineering Chemistry*, 39:1543-1548.
- Demirbas A. and eKara H. (2006). New options for conversion of vegetable oils to alternative fuels, *Energy Sources*, 28: 619-626.

- FAO and Oil World (2014). *Food Outlook*. New York.
- Fu J, et al. (2010). Catalytic hydrothermal deoxygenation of palmitic acid. *The Journal of Energy and Environmental Science*, 3: 311 – 317.
- Fu J, et al. (2011). Hydrothermal decarboxylation and hydrogenation of fatty acids over Pt/C. *The Journal of Chem Sus Chem*, 4: 481 – 486.
- Honeywell UOP (2016). *Honeywell Green Jet Fuel*, <https://www.uop.com/processing-solutions/renewables/green-jet-fuel/>, 10/11/2016 2:59 PM.
- Kubickova I, et al. (2005). Hydrocarbons for diesel fuel via decarboxylation of vegetable oils, *Catalysis Today*, 106: 197 – 200.
- Ma'ki-Arvela P, et al. (2007). Catalytic Deoxygenation of Fatty Acids and Their Derivatives, *Energy & Fuels*, 30 – 41.
- Ralston A. (1948). *Fatty acids and derivatives*. London: Chapman Hall Limi.
- Santilan-Jimenes, E. and Crocker M. (2012). Catalytic deoxygenation of fatty acids and their derivatives to hydrocarbon fuels via decarboxylation/decarbonylation, *J Chem Technol Biotechnol*, 87: 1041 – 1050.
- Snare M, et al. (2008). Catalytic deoxygenation of unsaturated renewable feedstocks for production of diesel fuel hydrocarbons, *Fuel*, 87: 933 – 945.
- Soerawidjaja T.H. (2013). *Posisi strategis minyak-lemak nabati di dalam panorama teknologi BBN cair dan ketahanan energy nasional*. Jakarta: Focus Group Discussion Puslitbang TKEBTKE – Balitbang ESDM.
- U.S.Department of Energy (2016). *Energy Efficiency and Renewable Energy Alternatives fuels data center*. http://www.afdc.energy.gov/fuels/emerging_hydrocarbon.html. 10/11/2016 3:07 PM.

ABOUT THE AUTHORS

Ir. Godlief Fredrik Neonufa, MT: Lecturer in the Department of Agriculture Product Technology, Universitas Kristen Artha Wacana, Kupang 85000 Indonesia. Now, as a doctoral student in the Department of Chemical Engineering, Institut Teknologi Bandung, Bandung 40132 Indonesia.

DR. Tatang Hernas Soerawidjaja: Assoc Professor in the Department of Chemical Engineering, Institut Teknologi Bandung, Bandung 40132. He is my Promotor.

DR. Tirta Prakoso: Assoc Professor in the Department of Chemical Engineering, Institut Teknologi Bandung, Bandung 40132. He is my Co-Promotor