Calcium Methoxide Synthesis from Quick Lime using as Solid Catalyst in Refined Palm Oil Biodiesel Production

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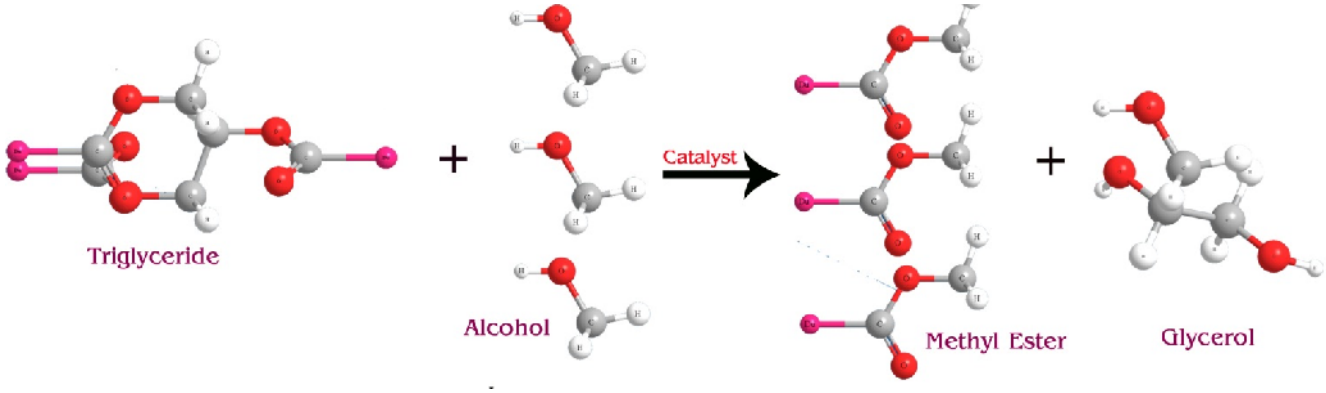
OUTLINE

- Introduction
- Objective
- Experimental
- Results & Discussion
- Conclusions

INTRODUCTION

INTRODUCTION

Transesterification



Catalyst

- Homogeneous catalyst
- Heterogeneous catalyst

http://www.scimath.org/socialnetwork/groups/viewbulletin/529-%E0%B8%9B%E0%B8%8F%E0%B8%BA%E0%B8%B4%E0%B8%81%E0%B8%B4%E0%B8%A3%E0%B8%B4%E0%B8%A2%E0%B8%B2%E0%B9%80%E0%B8%84%E0%B8%A1%E0%B8%B5%E0%B8%97%E0%B8%B5%E0%B9%88%E0%B9%80%E0%B8%81%E0%B8%B5%E0%B9%88%E0%B8%A2%E0%B8%A7%E0%B8%82%E0%B9%89%E0%B8%AD%E0%B8%87?groupid=166

INTRODUCTION

	Homogeneous	Heterogeneous
Separation and purification step	Complex	Simple
Waste	Salt and aqueous wastes	No waste stream
Chemicals	Consumption of chemical	No consumption
Costs and the environmental impact	High	Low

INTRODUCTION

Heterogeneous catalyst



Calcium methoxide as highly effective catalyst for biodiesel production

OBJECTIVE

To prepared calcium methoxide from quick lime and characterizations.

Investigated activity of solid base in reaction variables (amount of catalyst, methanol to oil molar ratio, reaction time) on the transesterification.

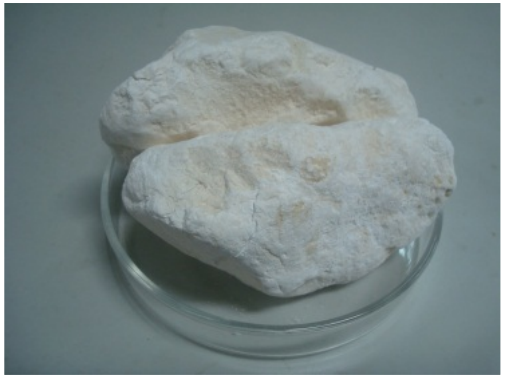
EXPERIMENTAL

Chemicals

1. Quick lime
2. Refined palm oil
3. Methanol (Analytical Grade)
4. FAME standard substance and solvents for GC

EXPERIMENTAL

Synthesis of catalyst



Quick lime was ground manually using mortar and pestle

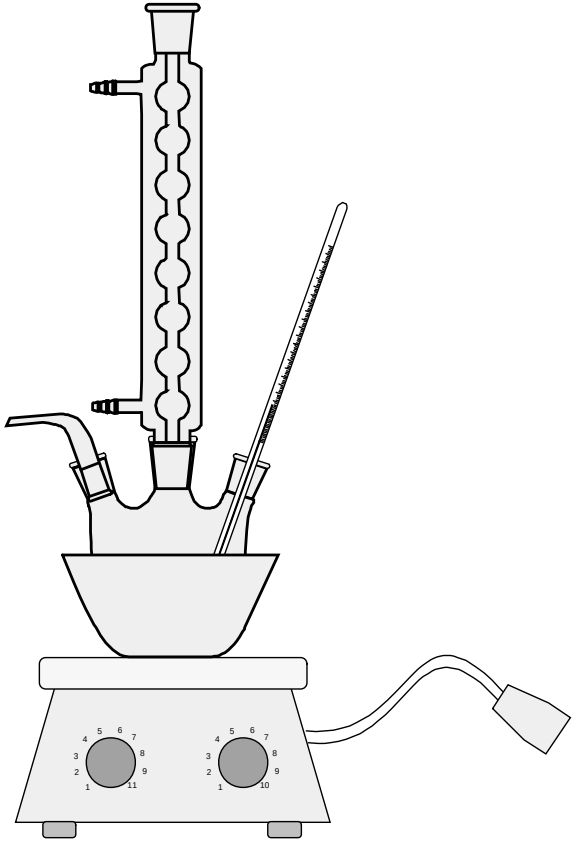
quick lime powder

EXPERIMENTAL

Synthesis of catalyst

quick lime powder

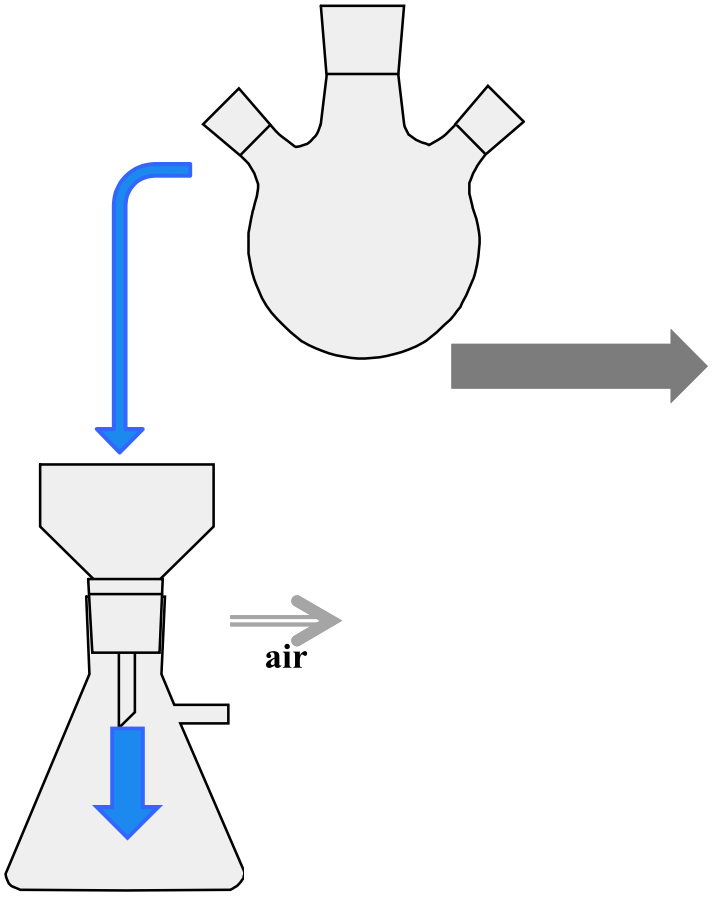
Calcine at 700 °C for 3.0 h



5g calcined product was reacted with 150 mL methanol under reflux at 65 °C for 2 h and continuous stirring 1500 rpm

EXPERIMENTAL

Synthesis of catalyst

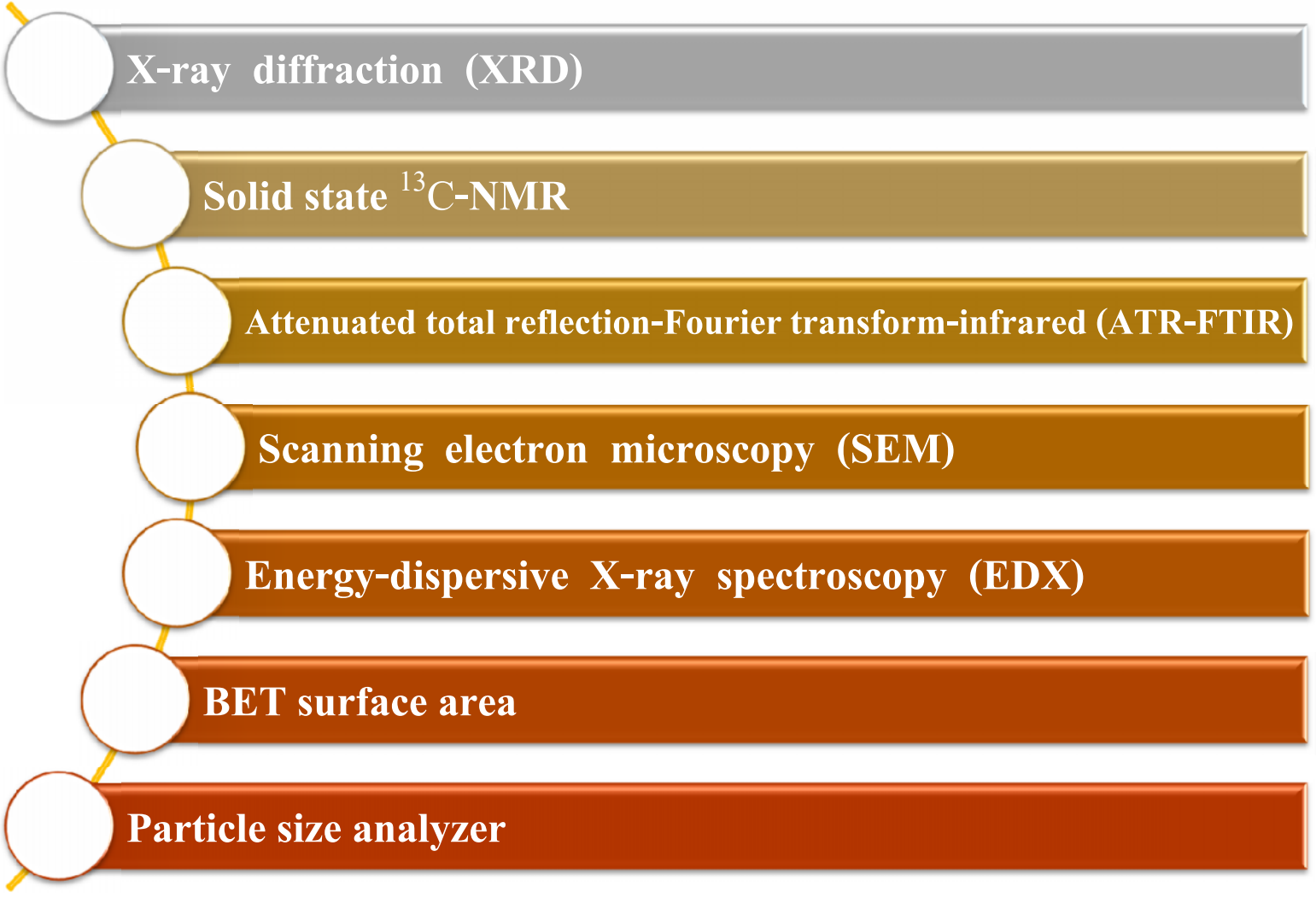


Dried in the oven at

105 °C for 1 h

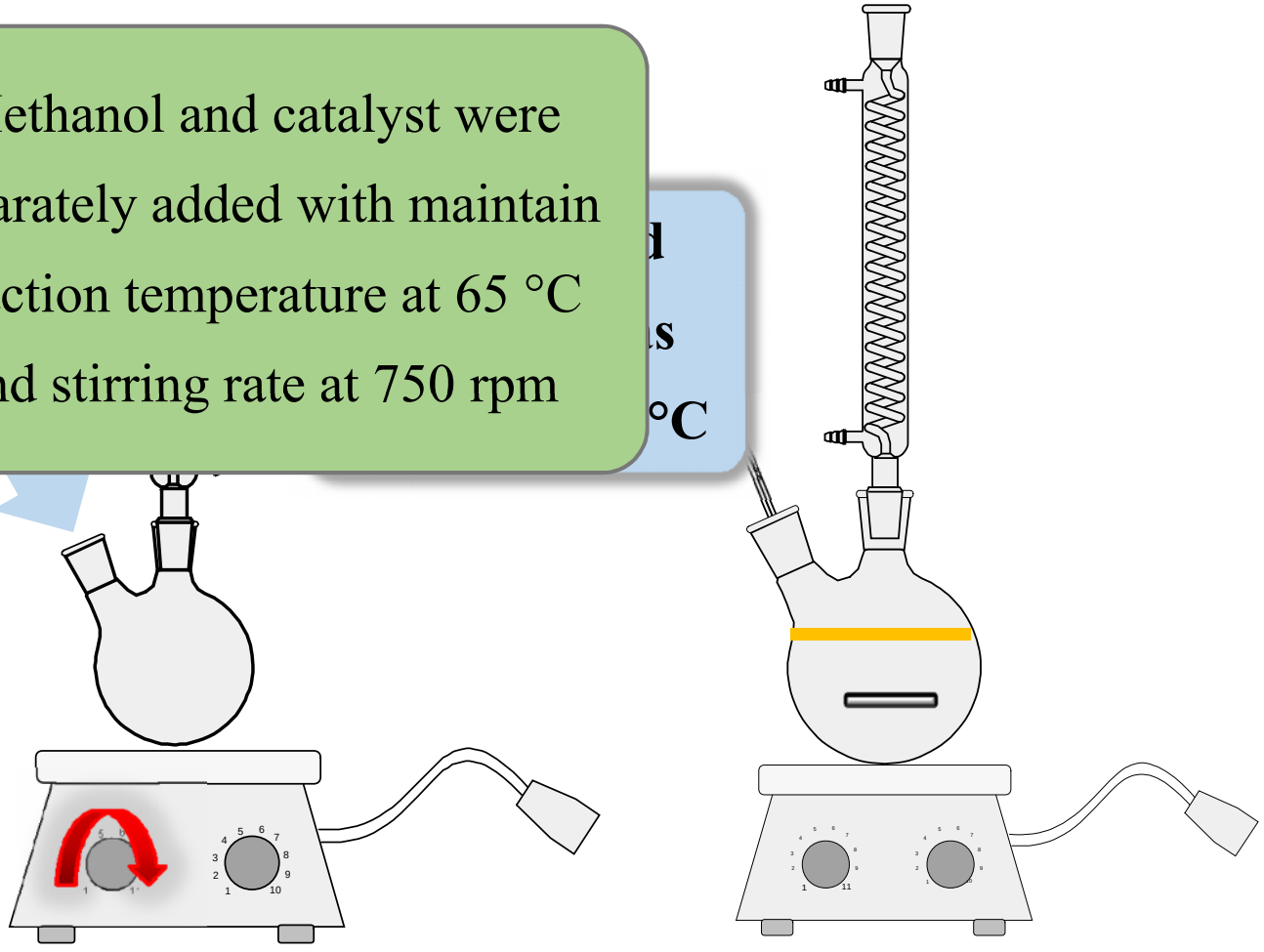
EXPERIMENTAL

Catalyst characterization



Transesterification reaction

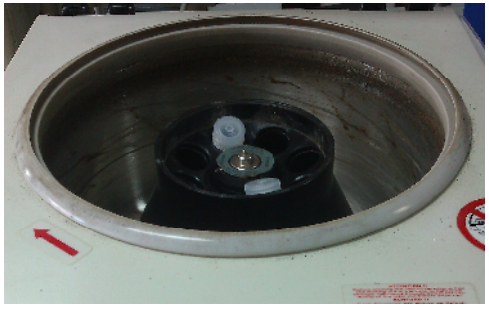
Methanol and catalyst were separately added with maintain reaction temperature at 65 °C and stirring rate at 750 rpm



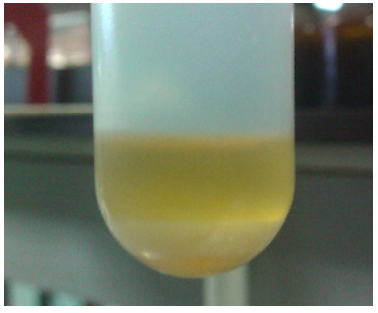
EXPERIMENTAL

FAME analysis

The reaction mixture was centrifuged



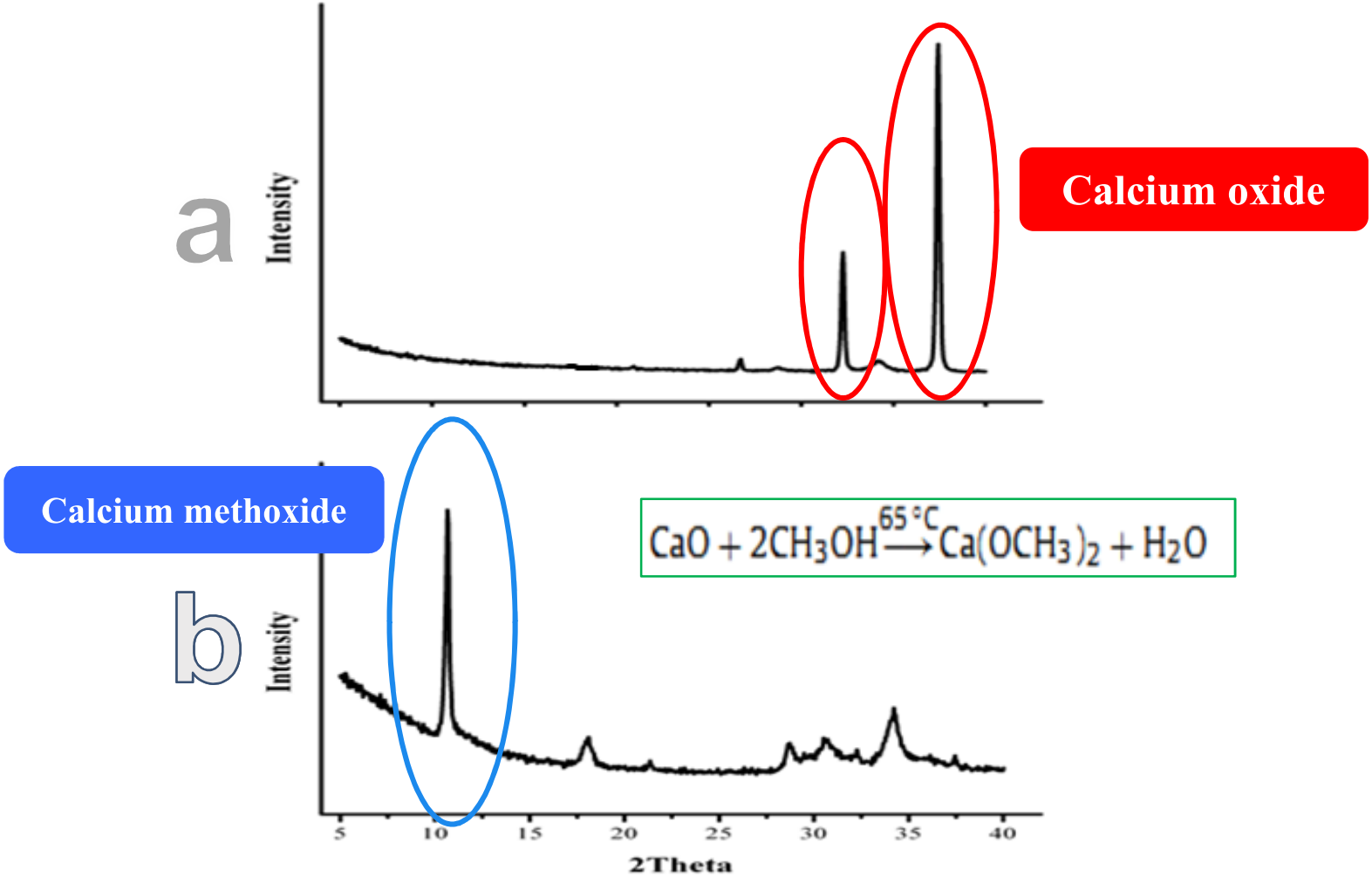
The biodiesel was collected from the products were centrifuged



The biodiesel was analyzed by gas chromatography (GC)

RESULTS & DISCUSSION

Characterizations of the synthesized catalyst

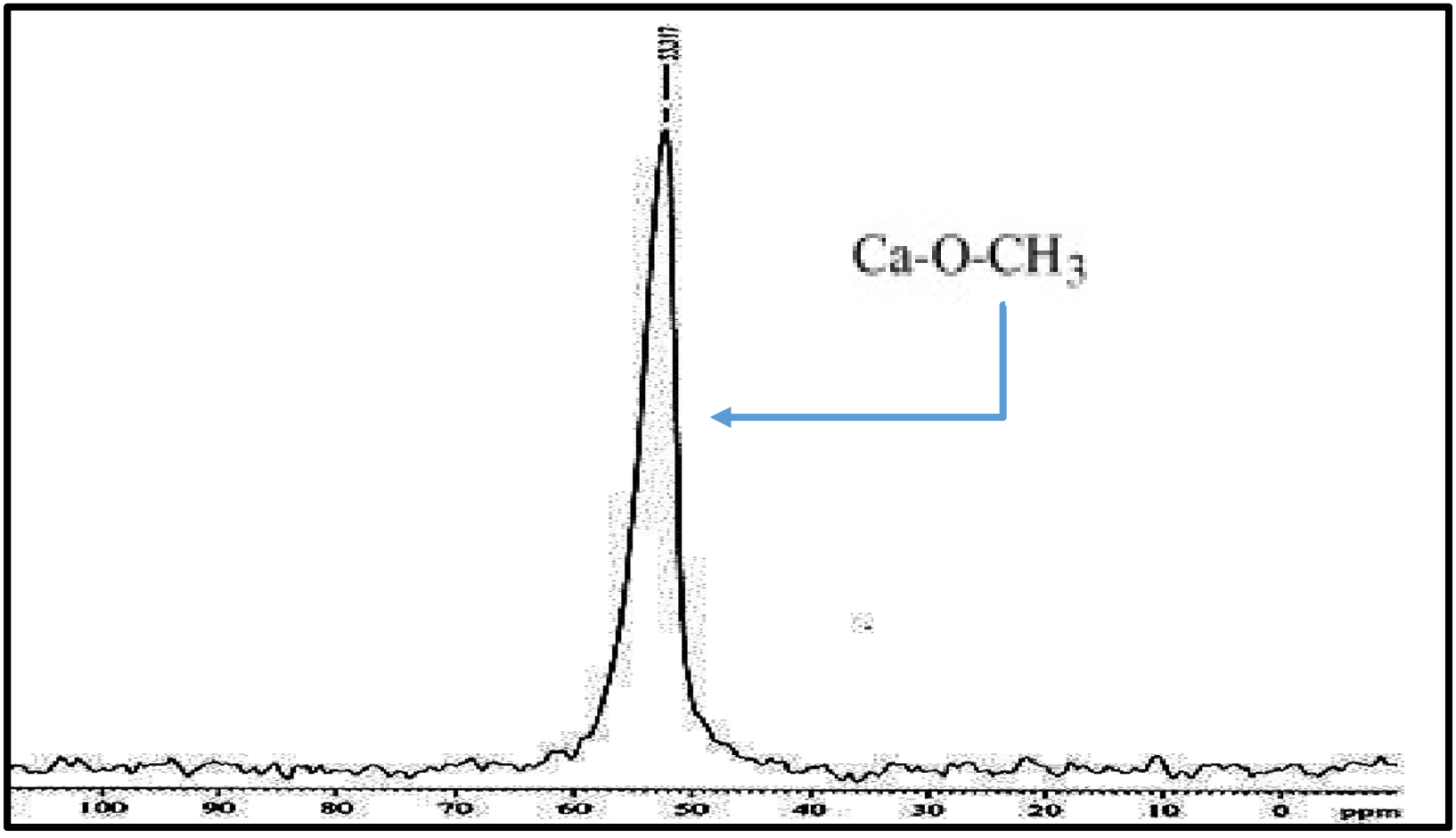


$$CaO + 2CH_3OH \xrightarrow{65\,^{\circ}C} Ca(OCH_3)_2 + H_2O$$

1. XRD patterns of (a) calcined quick lime; (b) reaction product.

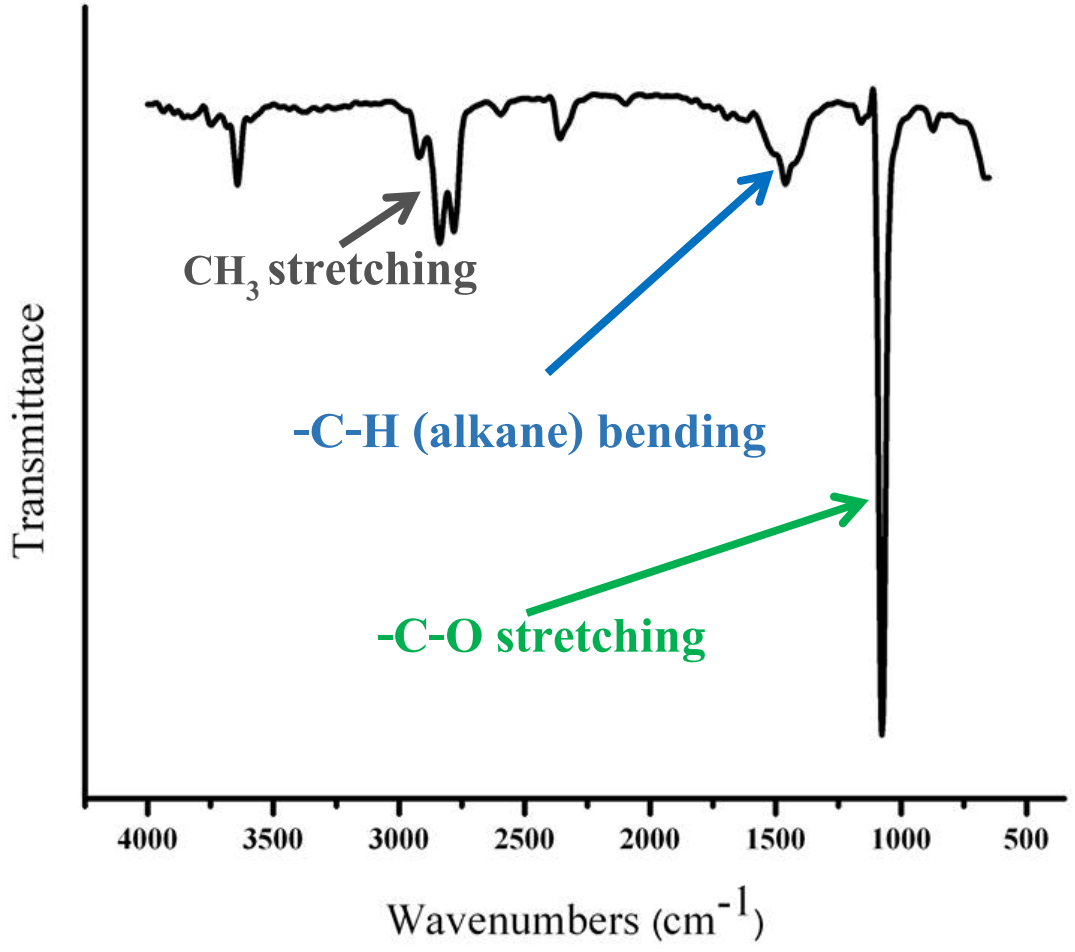
RESULTS & DISCUSSION

Characterizations of the synthesized catalyst



2. Spectra of solid state ^{13}C-NMR of calcium methoxide.

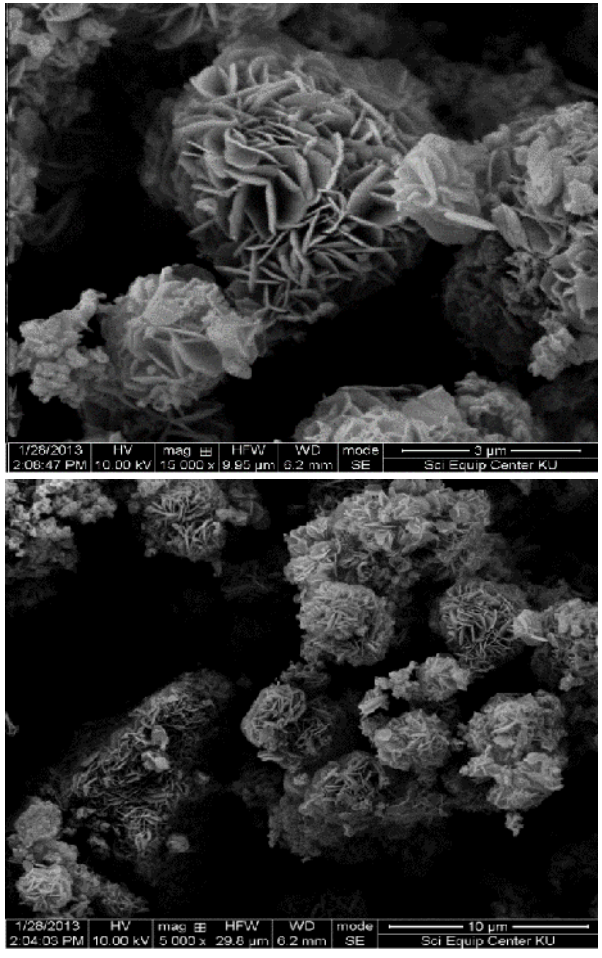
Characterizations of the synthesized catalyst

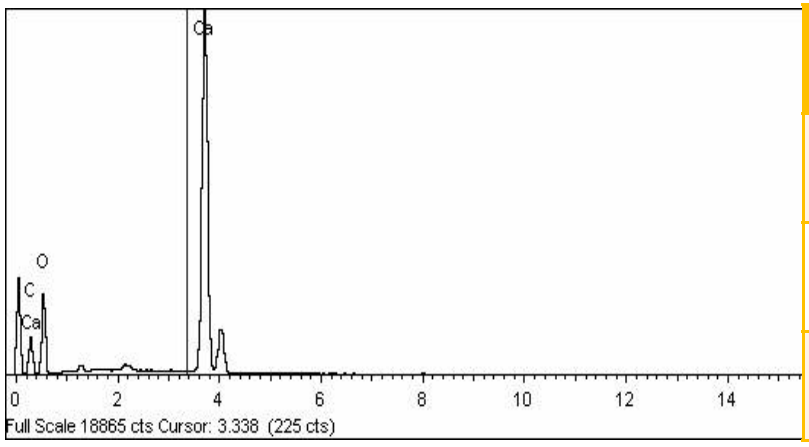


3. FTIR spectrum of calcium methoxide.

RESULTS & DISCUSSION

Characterizations of the synthesized catalyst





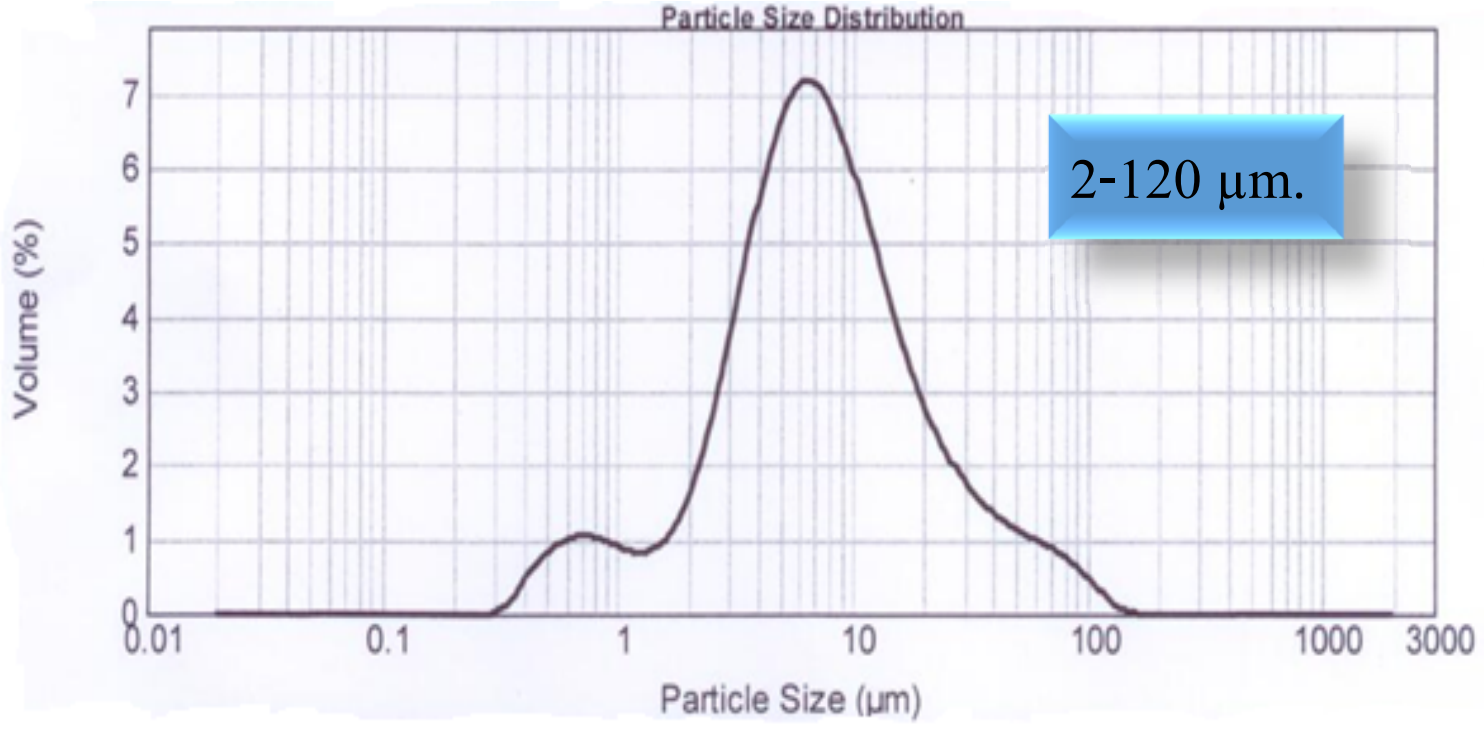
Element
Ca
O
C

Properties	results
BET surface area (m^2/g)	38.46
Total pore volume (cm^3/g)	0.33
Average pore diameter (nm)	34.39

4. SEM images, EDX spectrum and BET of calcium methoxide.

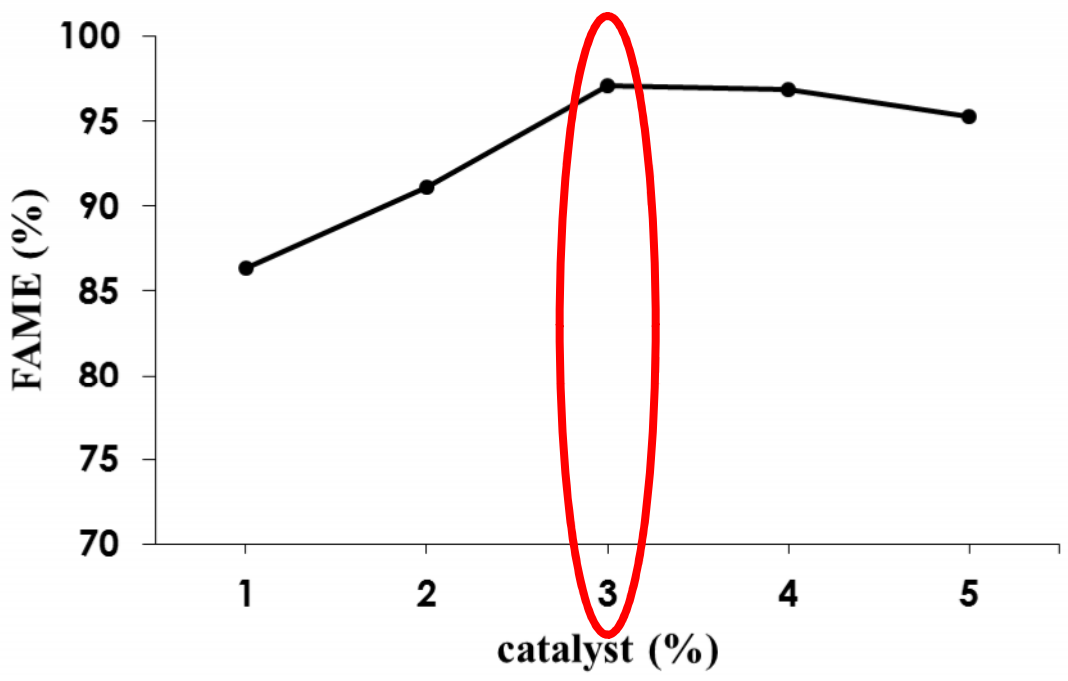
RESULTS & DISCUSSION

Characterizations of the synthesized catalyst



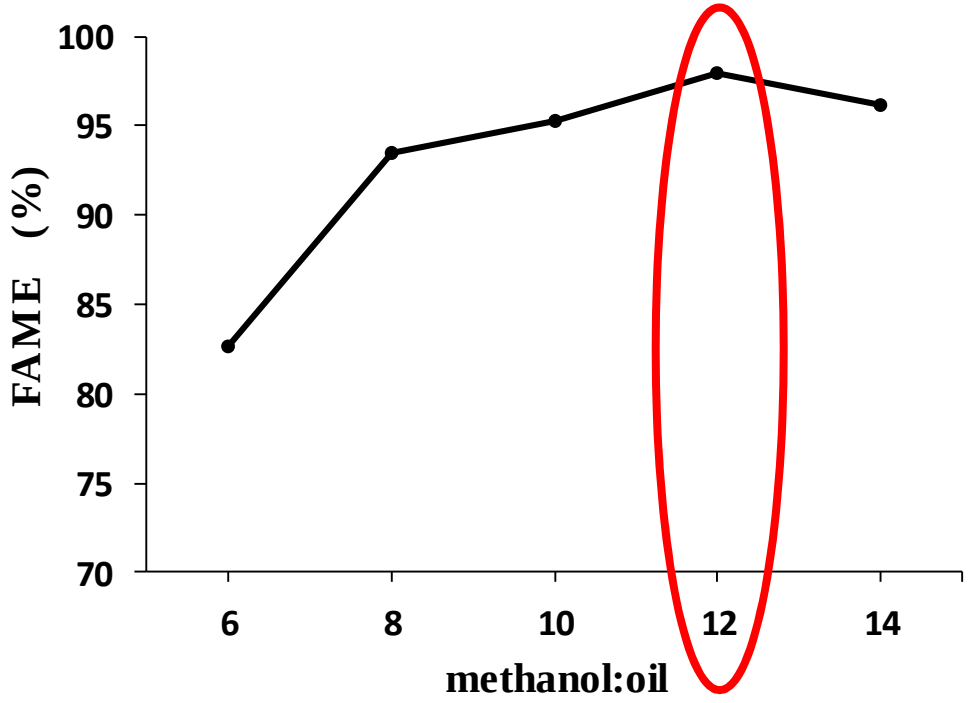
5. Particle size distribution of calcium methoxide.

Transesterification reaction



6. Effect of catalyst concentration on FAME(%), reaction time, 3h ; methanol:oil molar ratio, 12:1 ; reaction temperature, 65 °C.

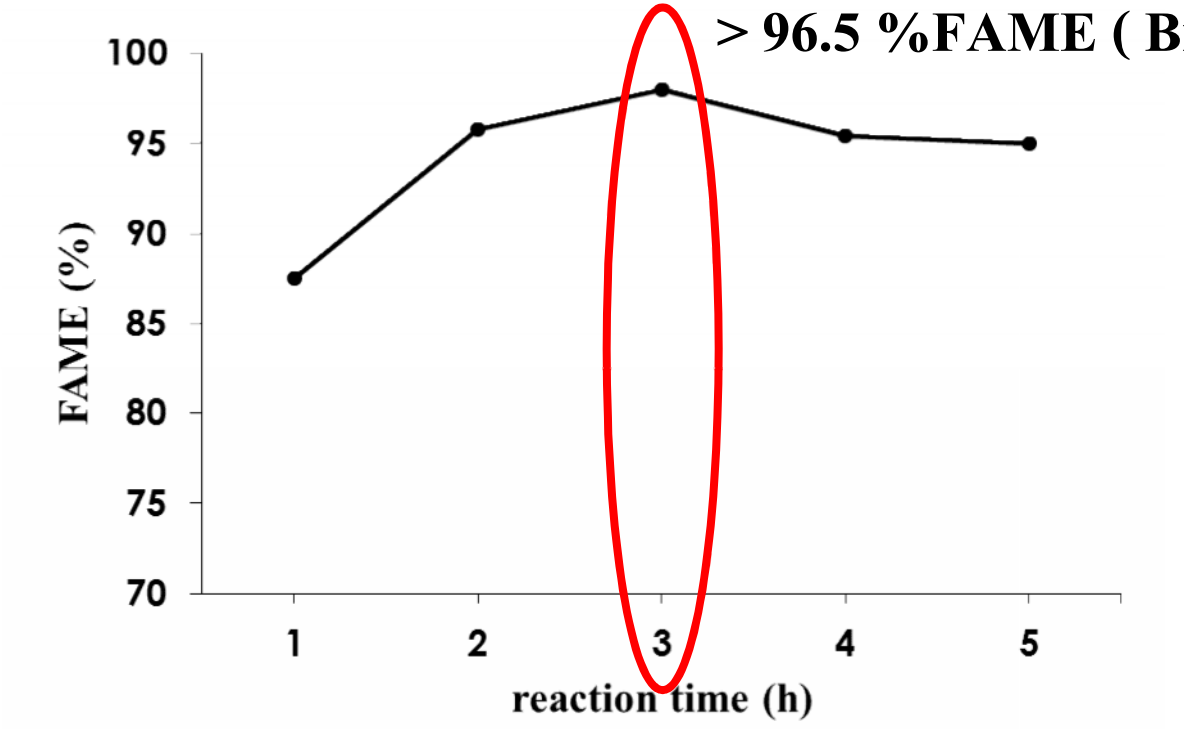
Transesterification reaction



7. Effect of methanol to oil molar ratio on FAME(%), catalyst concentration, 3% ; reaction time, 3h ; reaction temperature, 65 °C.

RESULTS & DISCUSSION

Transesterification reaction



8. Effect of reaction time on FAME(%), catalyst concentration, 3% ; methanol:oil molar ratio, 12:1; reaction temperature, 65 °C.

CONCLUSIONS

The solid state ^{13}C-NMR, XRD, ATR-FTIR, SEM and EDX results showed that the catalyst was successfully synthesized with sufficient purity.

The experimental results showed good catalytic ability of calcium methoxide for the transesterification of refined palm oil with methanol.

Finally, calcium methoxide could potentially substitute liquid catalyst.

REFERENCE

Masood, H., R. Yunus, et al. 2012. Synthesis and characterization of calcium methoxide as heterogeneous catalyst for trimethylolpropane esters conversion reaction. **Applied Catalysis A: General** 425–426: 184-190.

Kouzu, M., M. Tsunomori, et al. 2010. Solid base catalysis of calcium oxide for a reaction to convert vegetable oil into biodiesel. **Advance Powder Technology**. 21: 488–494.

Liu, X., X. Piao, Y. Wang, S. Zhu and H. He. 2008. Calcium methoxide as a solid base catalyst for the transesterification of soybean oil to biodiesel with methanol. **Fuel**. 87: 1076–1082.

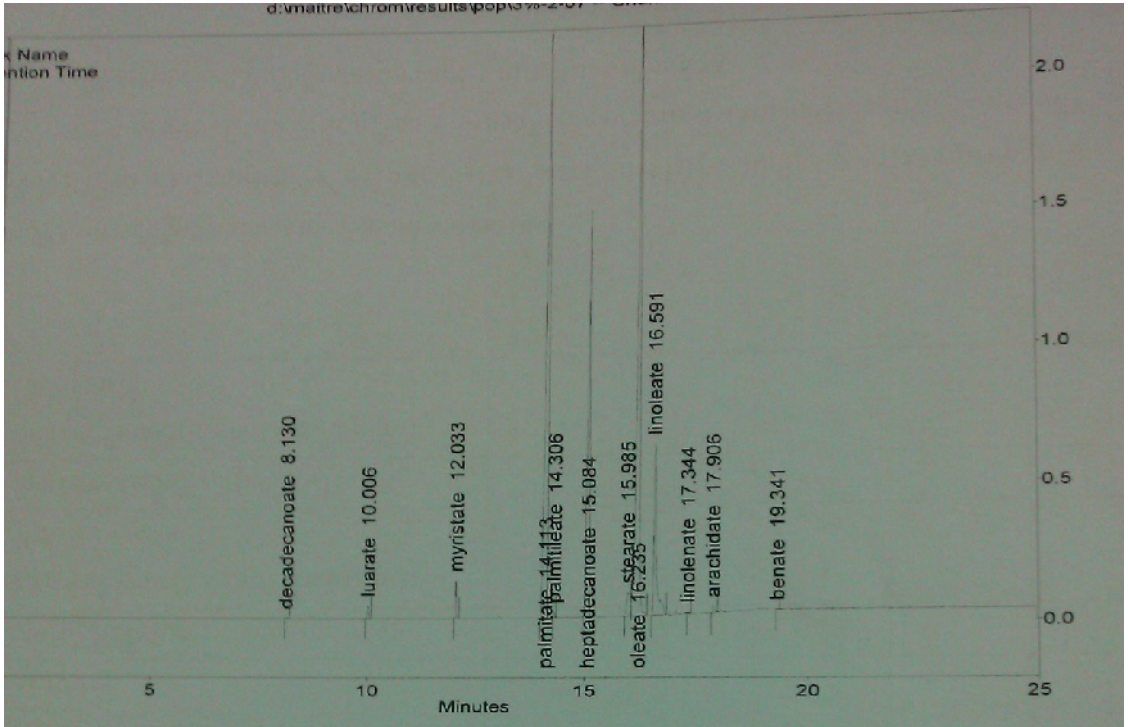
Thank you
For
Your attention

Questions

FAME analysis

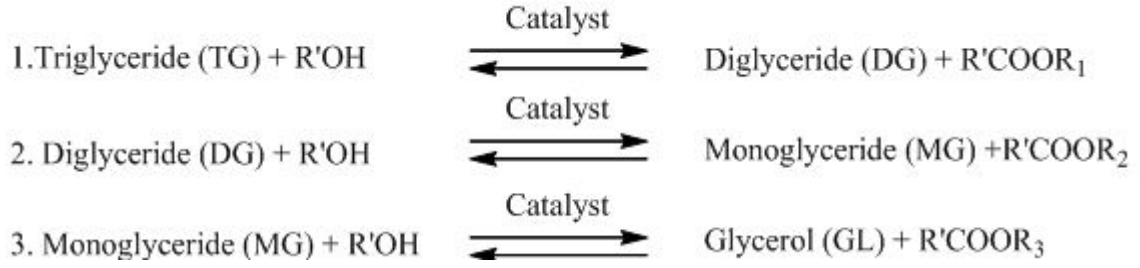
Calculation % Fatty acid methyl ester by GC

- Internal standard (C_{17})
- The capillary column (DB-WAX)
- Helium as carrier gas
- Oven temperature 250 °C



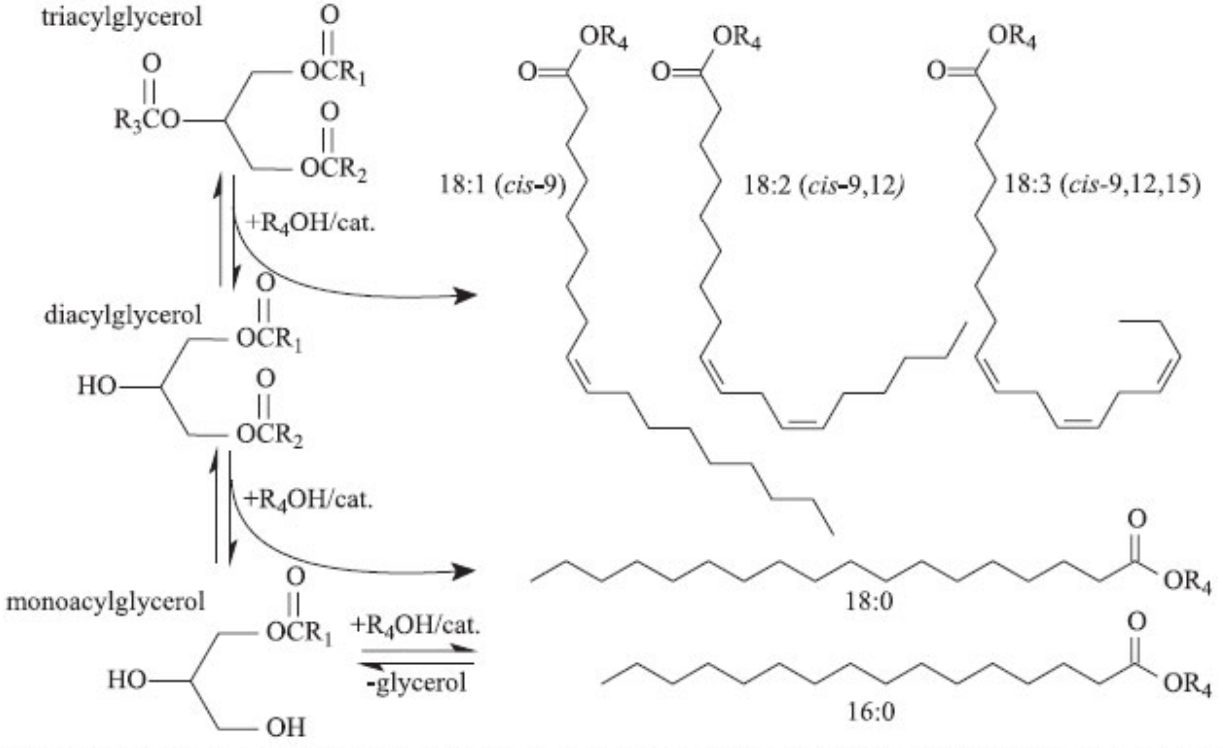
esults

RT(min)	Area	Area %	Name
4.749	0	0.000	octadecanoate
8.130	5436	0.019	decadecanoate
10.006	99650	0.357	luarate
12.033	237552	0.850	myristate
14.113	9937269	35.574	palmitate
14.306	34410	0.123	palmitileate
15.084	4770005	17.076	heptadecanoate
15.985	468023	1.675	stearate
16.235	9982619	35.736	oleate
16.591	2308090	8.263	linoleate
17.344	12674	0.045	linolenate
17.906	77316	0.277	arachidate
19.341	1081	0.004	benate
19.674	0	0.000	erucate
21.594	0	0.000	lignocerate
	27934124	100.000	



Biodiesel Fuel Production by Enzymatic Transesterification of Oils: Recent Trends, Challenges and Future Perspectives

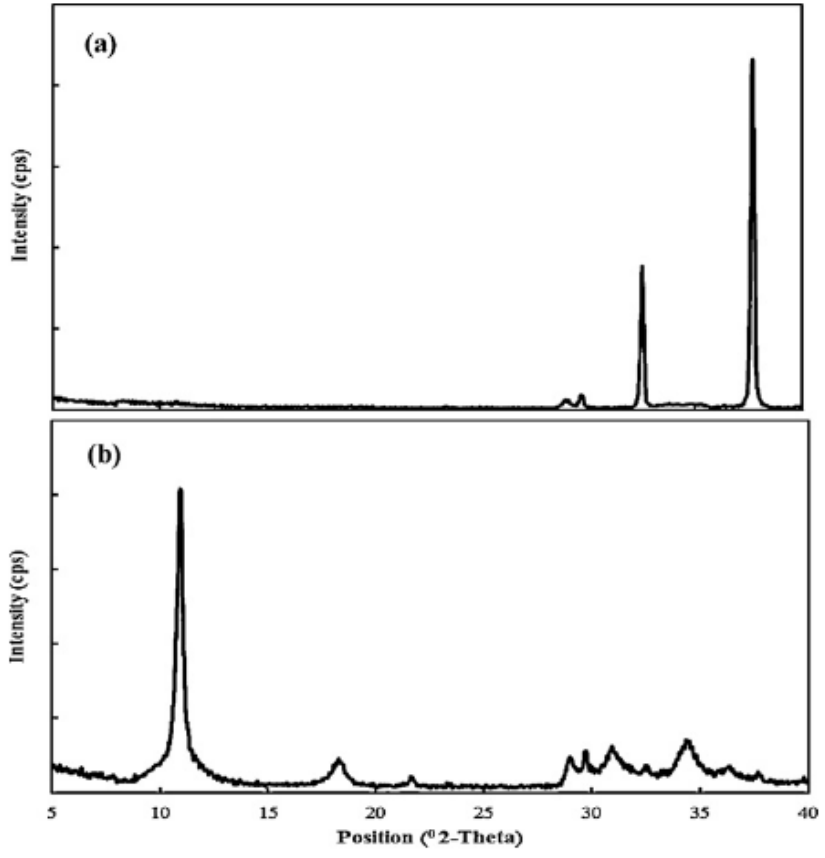
By Nevena Lukovic, Zorica Kneževic-Jugovic and Dejan Bezbradica

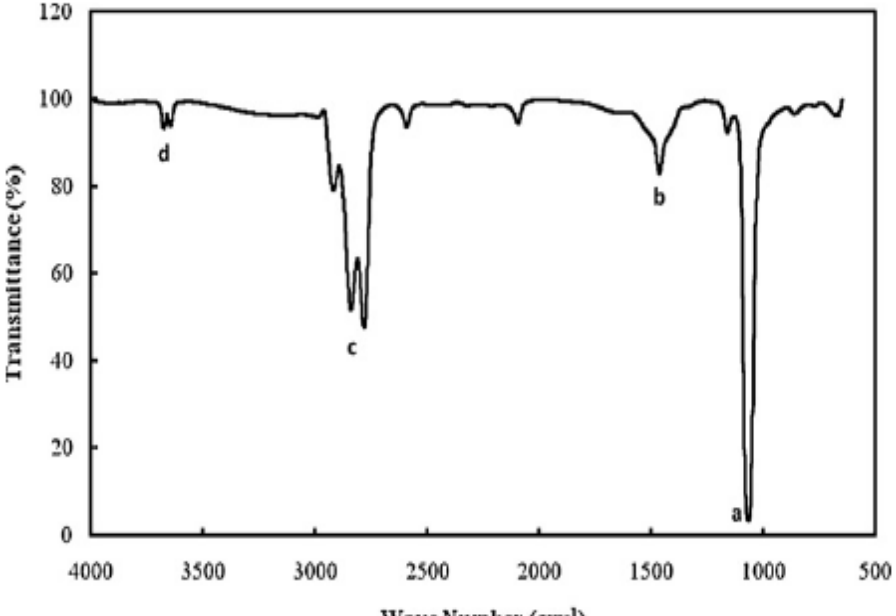


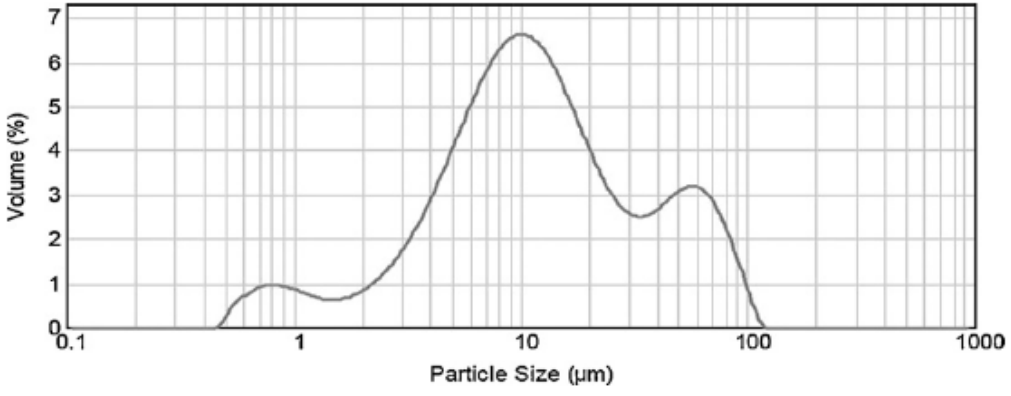
Scheme 1. Transesterification of triacylglycerol (any feedstock). R_1, R_2 and R_3 are the carbon chains of aliphatic esters and R_4 are of alcohols. It is illustred the main fatty acid esters in oils used in this work: palmitic (16:0), estearic (18:0), oleic (18:1), linoleic (18:2) and linolenic (18:3).

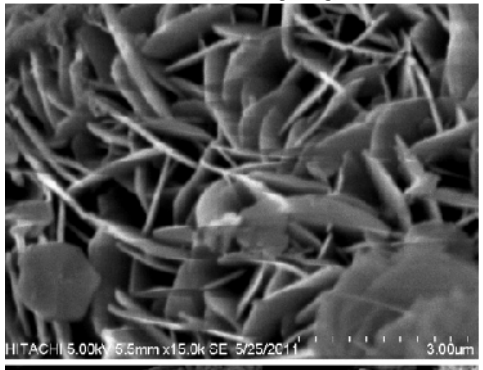
Chromatographic analyses of fatty acid methyl esters by HPLC-UV and GC-FID

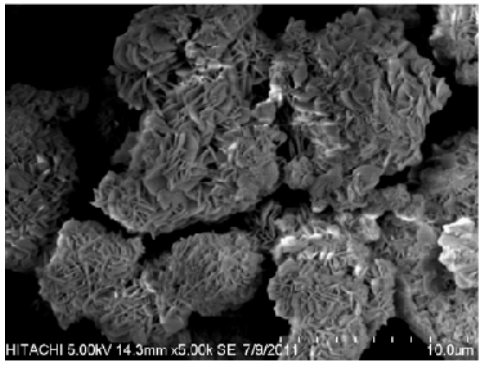
Myller S. Carvalho[I]; Márcio A. Mendonça[II]; David M. M. Pinho[I]; Inês S. Resck[III]; Paulo A. Z. Suarez[*,I]

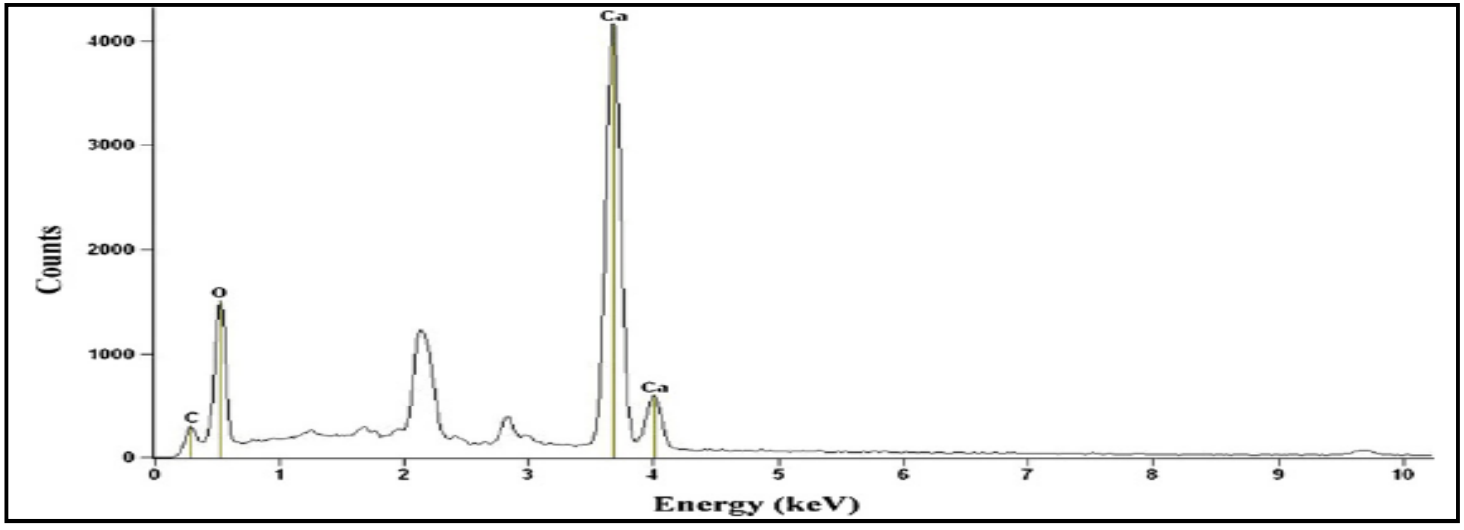

(a)
Intensity (cps)
(b)
Intensity (cps)
5
10
15
20
25
30
35
40
Position (°2-Theta)


120
100
80
60
40
20
0
Transmittance (%)
d
c
b
a
4000
3500
3000
2500
2000
1500
1000
500
Wave Number (cm-1)


7
6
5
4
3
2
1
0
Volume (%)
0.1
1
10
100
1000
Particle Size (μm)


HITACHI 5.00kV 5.5mm x15.0k SE 5/25/2011
3.00um


HITACHI 5.00kV 14.3mm x5.00k SE 7/8/2011
10.0um


Ca
4000
3000
2000
1000
0
Counts
O
C
Ca
0
1
2
3
4
5
6
7
8
9
10
Energy (keV)

Liu *et al.* (2008)

$$Ca + 2CH_3OH \xleftrightarrow{65\ ^\circ C,\ 4\ h} Ca(OCH_3)_2 + H_2$$

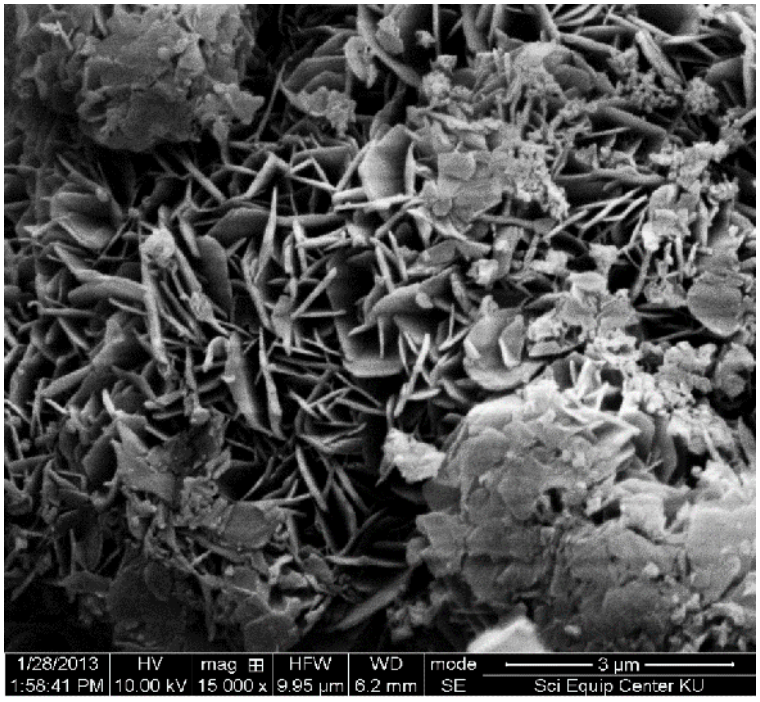
Fatty acid methyl ester yield = 98.00 % after 2 h.

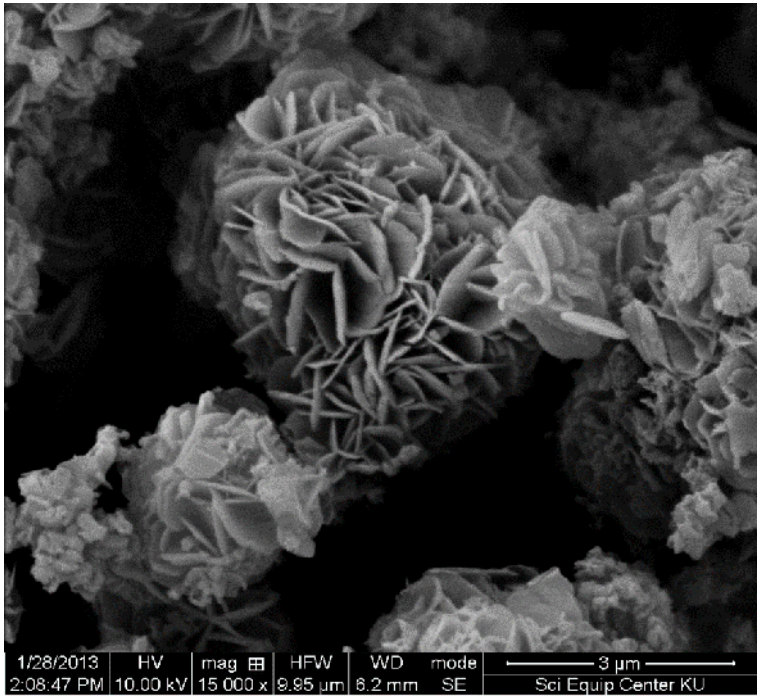
Masood *et al.* (2012)

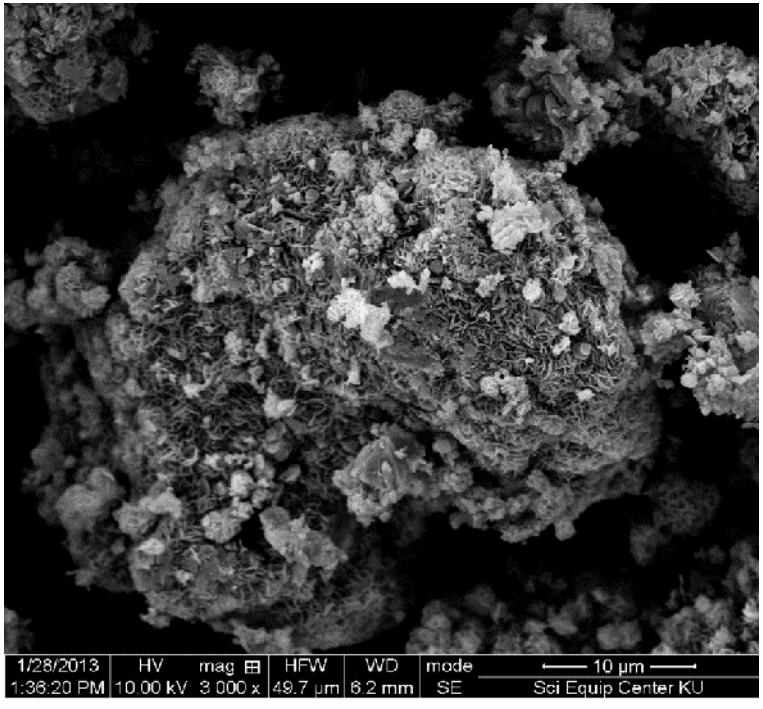
$$CaCO_3 \xleftrightarrow{900\ ^\circ C,\ 2h} CaO + CO_2$$

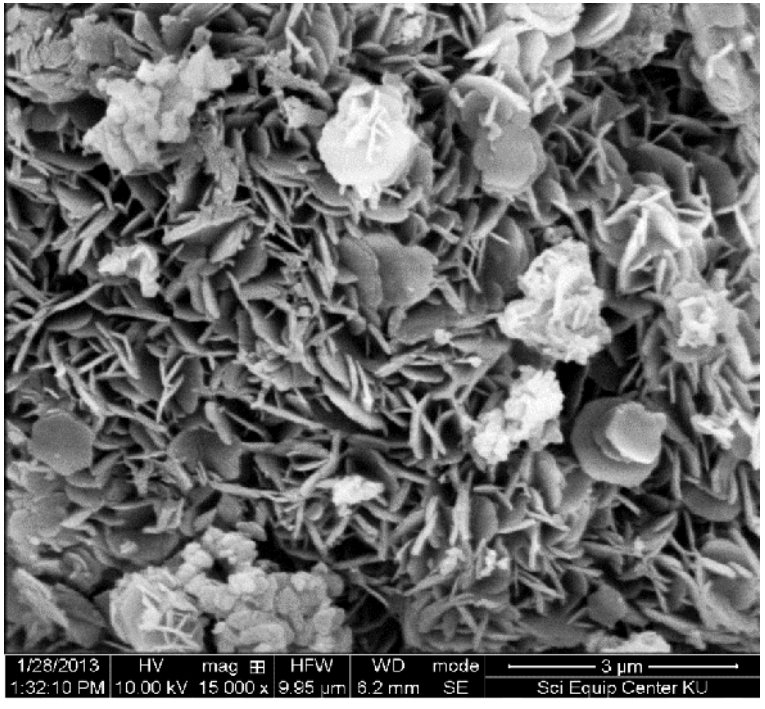
$$CaO + 2CH_3OH \xleftrightarrow{65\ ^\circ C,\ 2\ h} Ca(OCH_3)_2 + H_2O$$

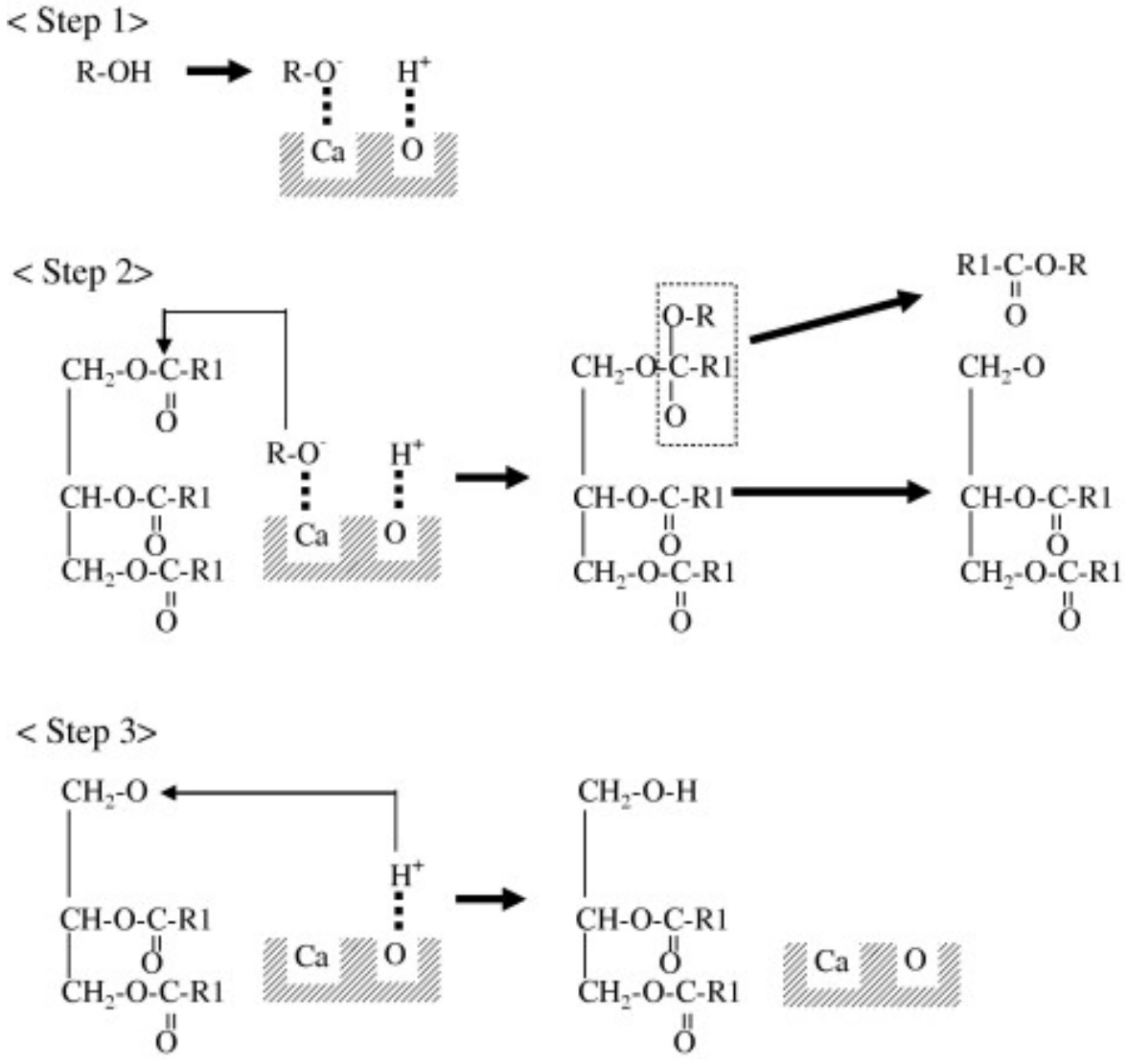
Trimethylolpropane ester yield = 92.38 % after 8 h.


1/28/2013 | HV | mag | HFW | WD | mode | 3 µm
1:58:41 PM | 10.00 kV | 15 000 x | 9.95 µm | 6.2 mm | SE | Sci Equip Center KU


1/28/2013 | HV | mag | HFW | WD | mode | 3 µm
2:08:47 PM | 10.00 kV | 15 000 x | 9.95 µm | 6.2 mm | SE | Sci Equip Center KU

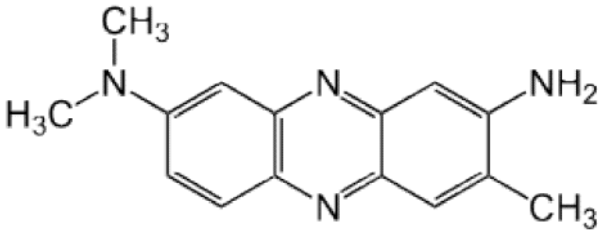

1/28/2013 | HV | mag | HFW | WD | mode | 10 µm
1:36:20 PM | 10.00 kV | 3 000 x | 49.7 µm | 6.2 mm | SE | Sci Equip Center KU


1/28/2013 | HV | mag | HFW | WD | mode | 3 µm
1:32:10 PM | 10.00 kV | 15 000 x | 9.95 µm | 6.2 mm | SE | Sci Equip Center KU



Reaction route of transesterification of triglyceride with methanol using CaO.

3-Amino-7-dimethylamino-2-methylphenazine hydrochloride

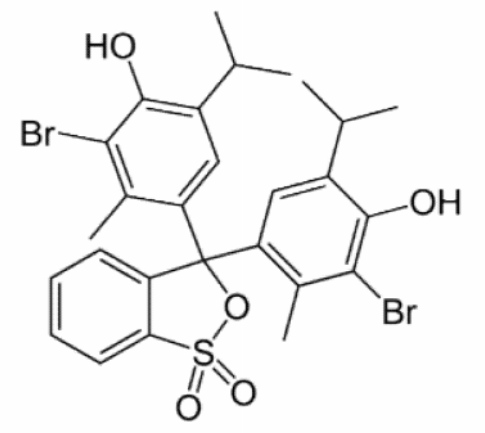


Neutral red (pH indicator)

below pH 6.8 *above pH 8.0*

6.8 ↔ 8.0

4,4'-(1,1-dioxido-3*H*-2,1-benzoxathiole-3,3-diyl)bis(2-bromo-6-isopropyl-3-methylphenol)

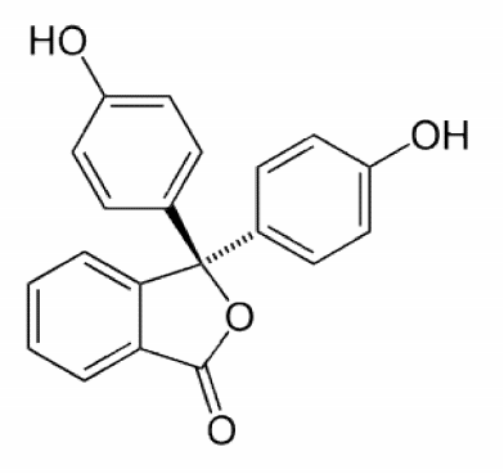


Bromothymol Blue (pH indicator)

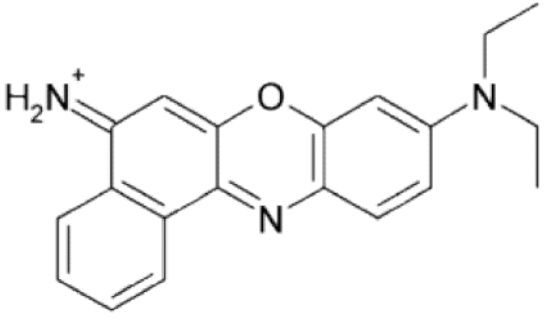
below pH 6.0 *above pH 7.6*

6.0 ↔ 7.6

3,3-bis(4-hydroxyphenyl)isobenzofuran-1(3*H*)-one

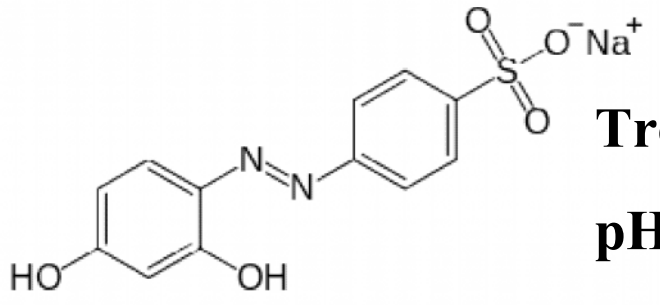


Phenolphthalein (pH indicator)		
below pH 8.2		*above pH 10.0*
colorless	⇌	fuchsia



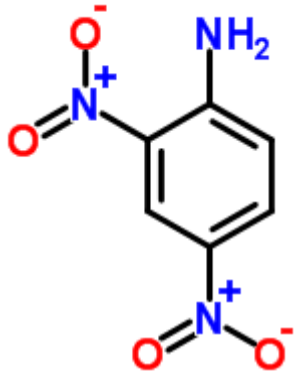
Nile blue in water.

Left to right: pH 0, pH 4, pH 7, pH 10, pH 14.

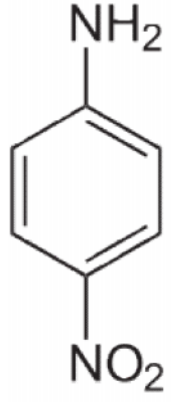


Tropaeolin O (H_ = 11.1) /

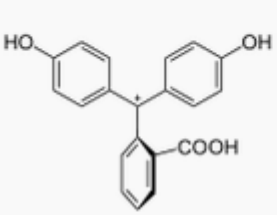
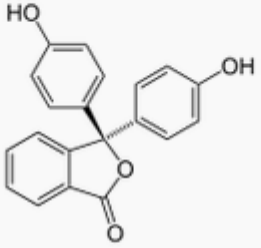
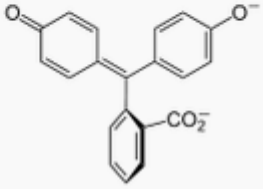
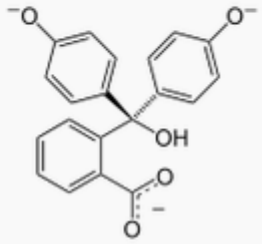
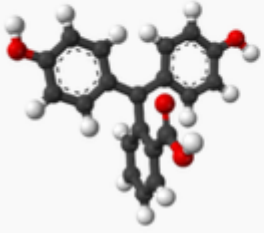
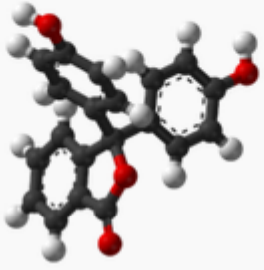
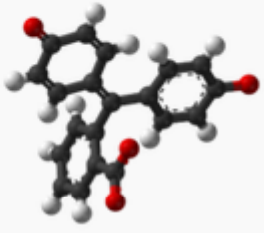
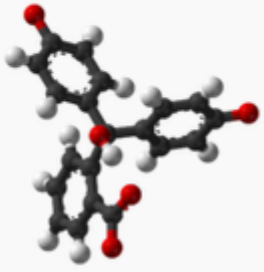
pH 11.1 (yellow) to pH 12.7 (orange)

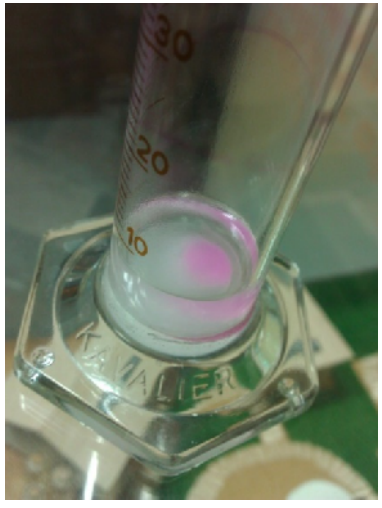


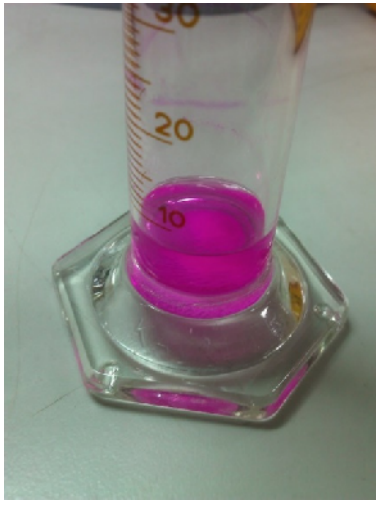
2,4-Dinitroaniline (H_ = 15) / Yellow - Violet



4-Nitroaniline (H_ = 18.4) / Yellow - Orange

Species	H_3In^+	H_2In	In^{2-}	$In(OH)^{3-}$
Structure				
Model				
pH	<0	0–8.2	8.2–12.0	>12.0
Conditions	strongly acidic	acidic or near-neutral	basic	strongly basic
Color	orange	colorless	pink to fuchsia	colorless
Image				


30
20
10


30
20
10

The Hammett acidity function, H_0, can replace the pH in concentrated solutions. It is defined using an equation analogous to the Henderson-Hasselbalch equation:

$$H_0 = \mathrm{p}K_{BH^+} + \log \frac{[B]}{[BH^+]}$$

where log(x) is the common logarithm of x, and $\mathrm{p}K_{\mathrm{BH}}^{+}$ is $-\log(K)$ for the dissociation of BH^+, which is the conjugate acid of a very weak base B, with a very negative $\mathrm{p}K_{\mathrm{BH}}^{+}$. In this way, it is rather as if the pH scale has been extended to very negative values. Hammett originally used a series of anilines with electron-withdrawing groups for the bases.

The indicator method, however, has disadvantages. Although the color change is assumed to be the result of an acid-base reaction, an indicator may change color by reactions different from the acid-base reaction. In addition, long time is required for benzoic acid to reach an adsorption equilibrium during titration carried out in a solution. In some cases, the surface of solid base catalysts may dissolve into the titration solution. If this occurs, the number of basic sites will be overestimated. Therefore, special care should be taken with the indicator method.

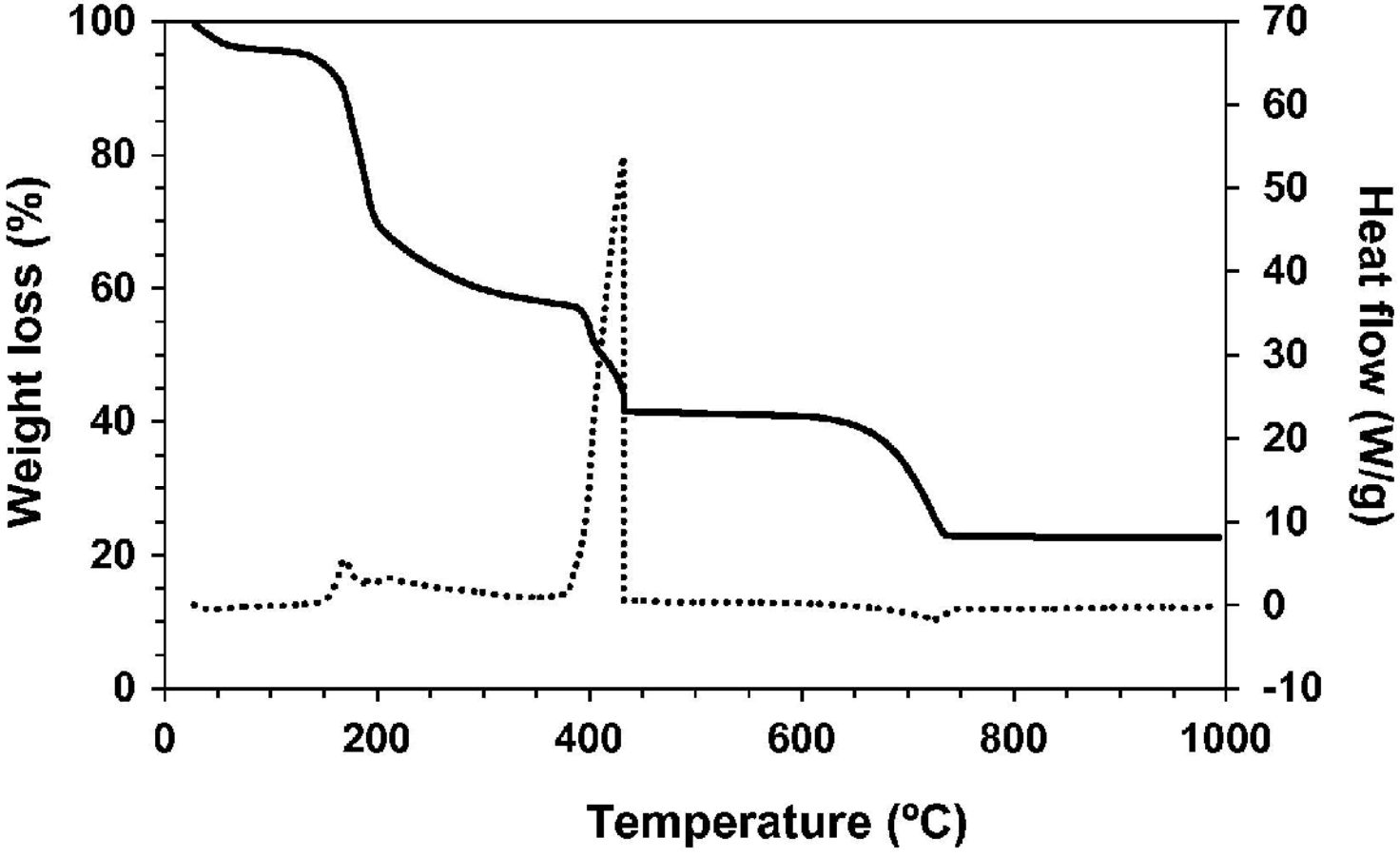
Table 1
Alkaline earth metal compound solubilities in methanol

Compound	MgO	$Ca(OH)_2$	CaO	$Ca(CH_3O)_2$	$Ba(OH)_2$
Solubility in methanol (%)	0.130	0.010	0.035	0.040 [a]	1.170

[a] Suspensoid.

$$Ca[O(OH)_2C_3H_5]_2 + 2CH_3OH \leftrightarrow Ca^{2+} + 2CH_3O^- + 2C_3H_5(OH)_3$$

the solubility of calciumglyceroxide inmethanolwas 6216mg/L



heat flow , J/s = W

Scherrer's Formula

$$t = \frac{K * \lambda}{B * \cos\theta_B}$$

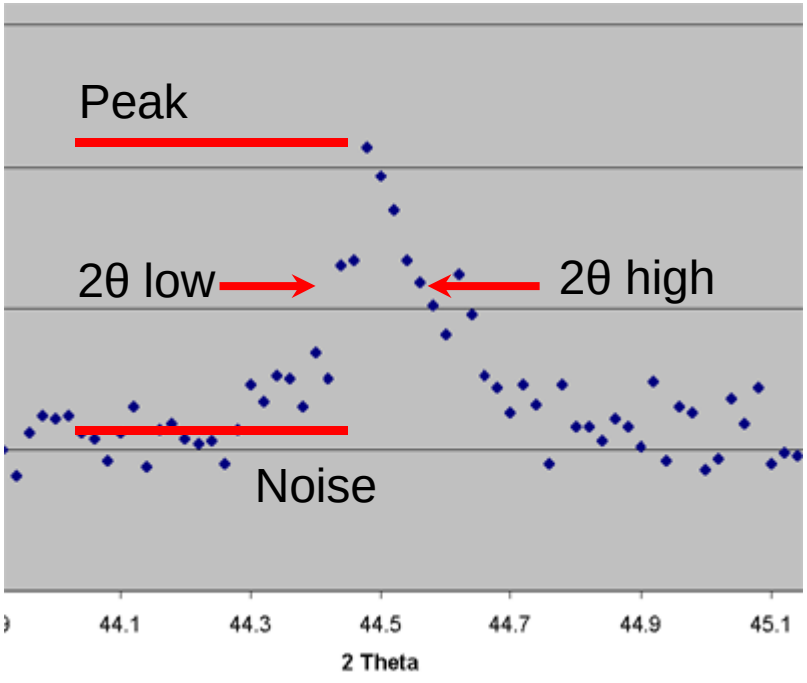
t = thickness of crystallite
K = constant dependent on crystallite shape (0.89)
λ = x-ray wavelength
B = FWHM (full width at half max) or integral breadth
θ_B = Bragg Angle

Scherrer's Formula

What is B?

$B = (2\vartheta \text{ High}) - (2\vartheta \text{ Low})$

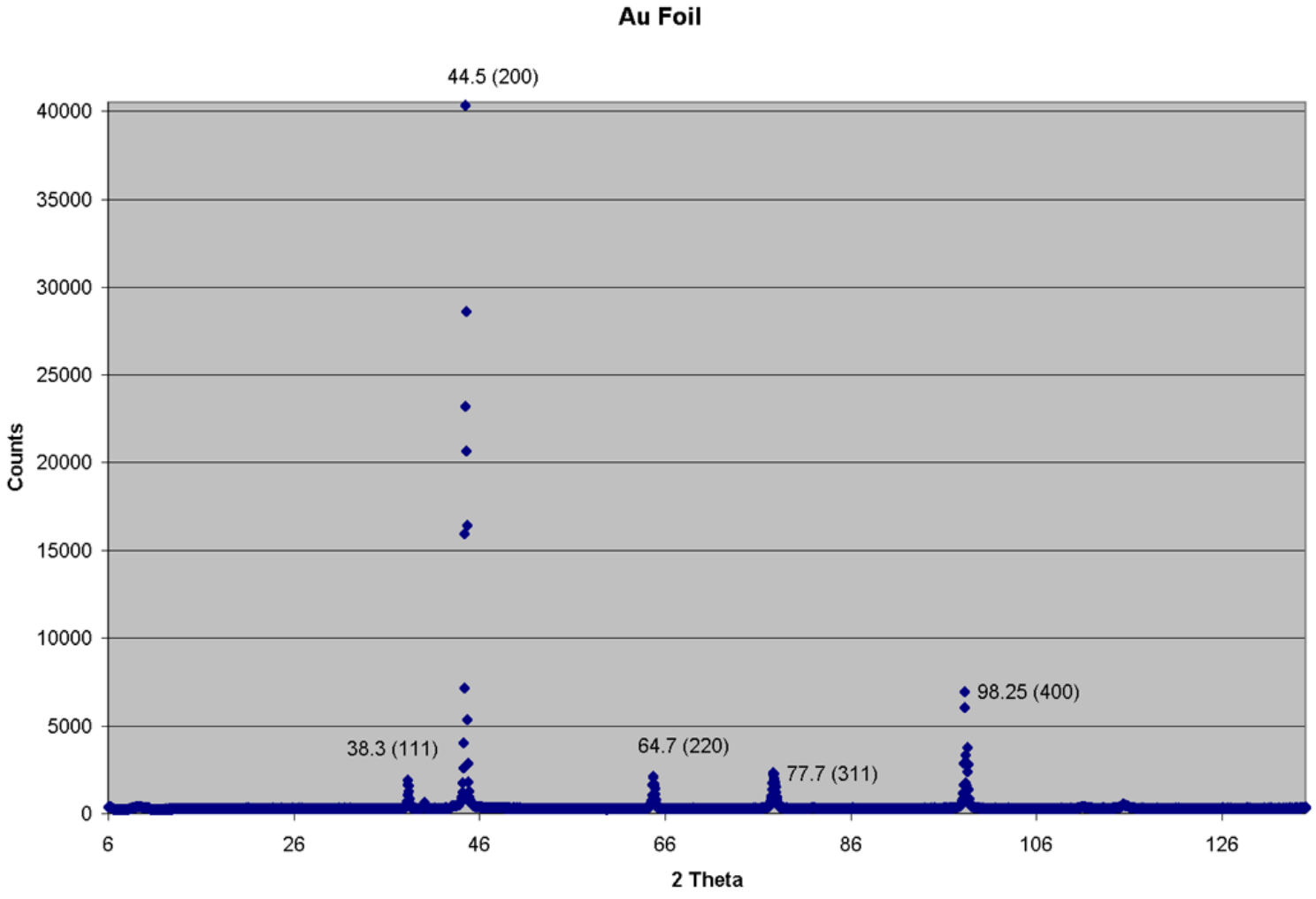
B is the difference in angles at half max



Data Analysis

- Plot the data (2ϑ vs. Counts)
- Determine the Bragg Angles for the peaks
- Calculate *d* and *a* for each peak
- Apply Scherrer's Formula to the peaks

Bragg Example



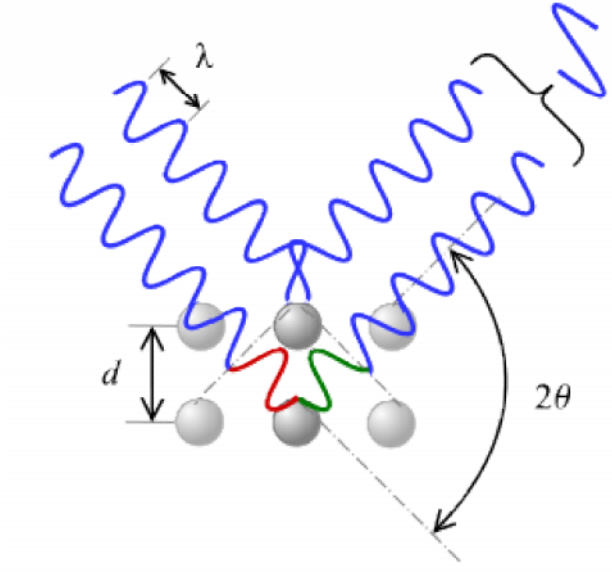
Bragg Example

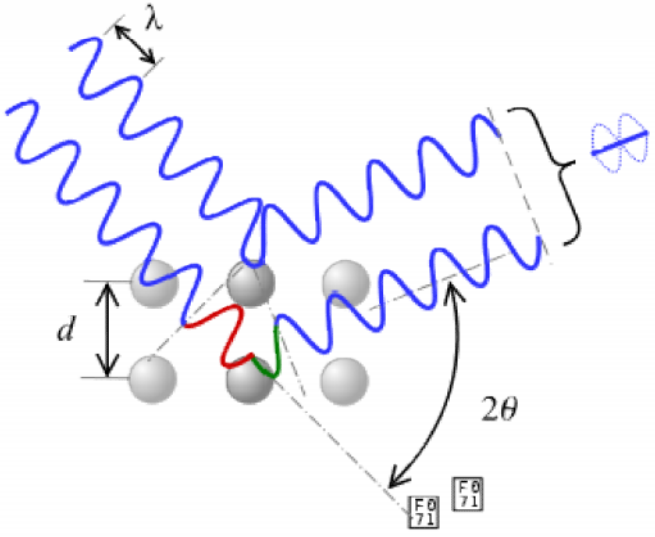
d $= \lambda / (2 \sin \theta_B)$ $\lambda = 1.54$ Å

$= 1.54$ Å $/ (2 * \sin (38.3 / 2))$

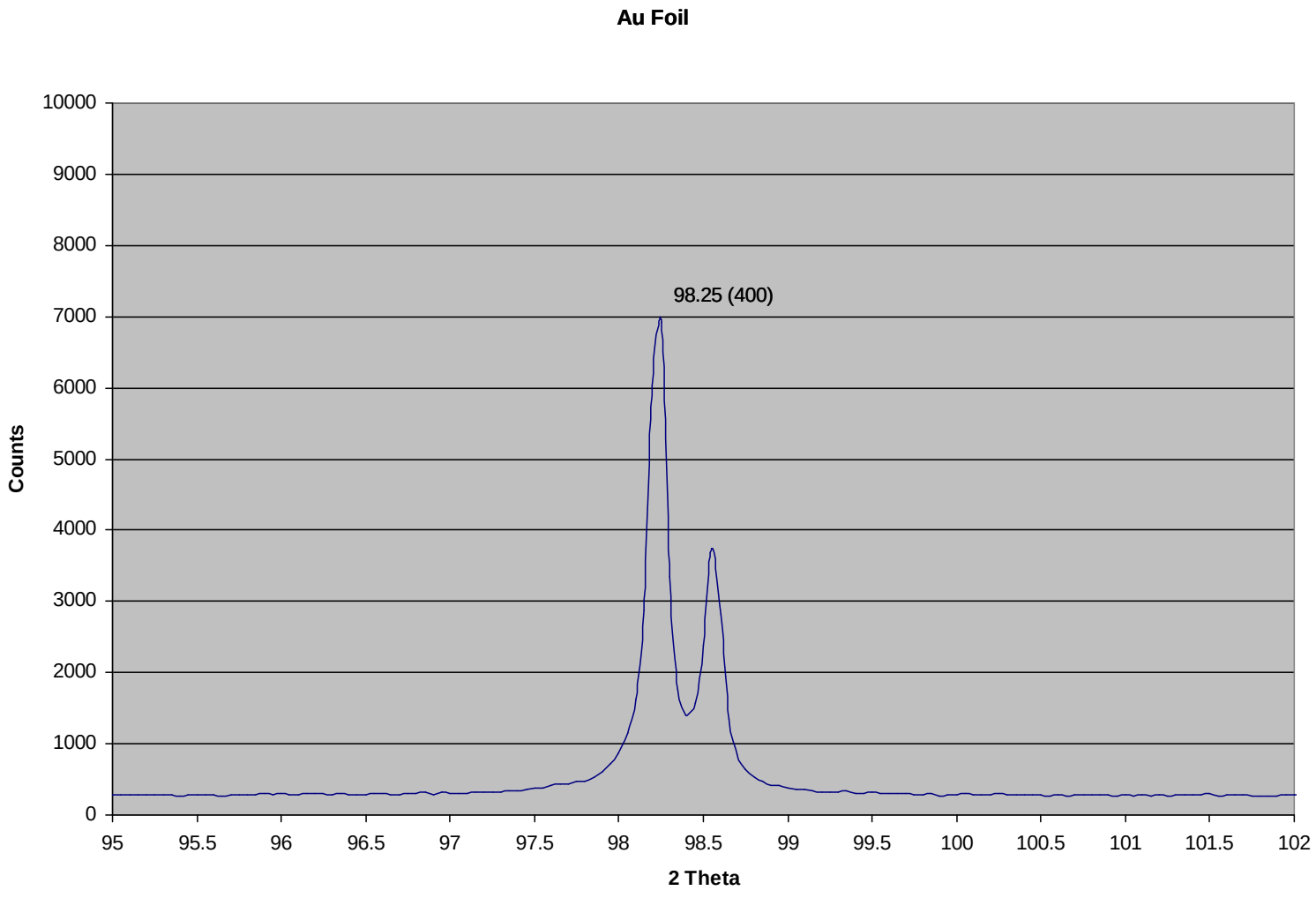
$= 2.35$ Å

Simple Right!





Scherrer's Example



Scherrer's Example

$$t = \frac{0.89 * \lambda}{B * \cos\theta_B}$$

t = 0.89*λ / (B Cos θ_B) λ = 1.54 Å

= 0.89*1.54 Å / (0.00174 * Cos (98.25/ 2))

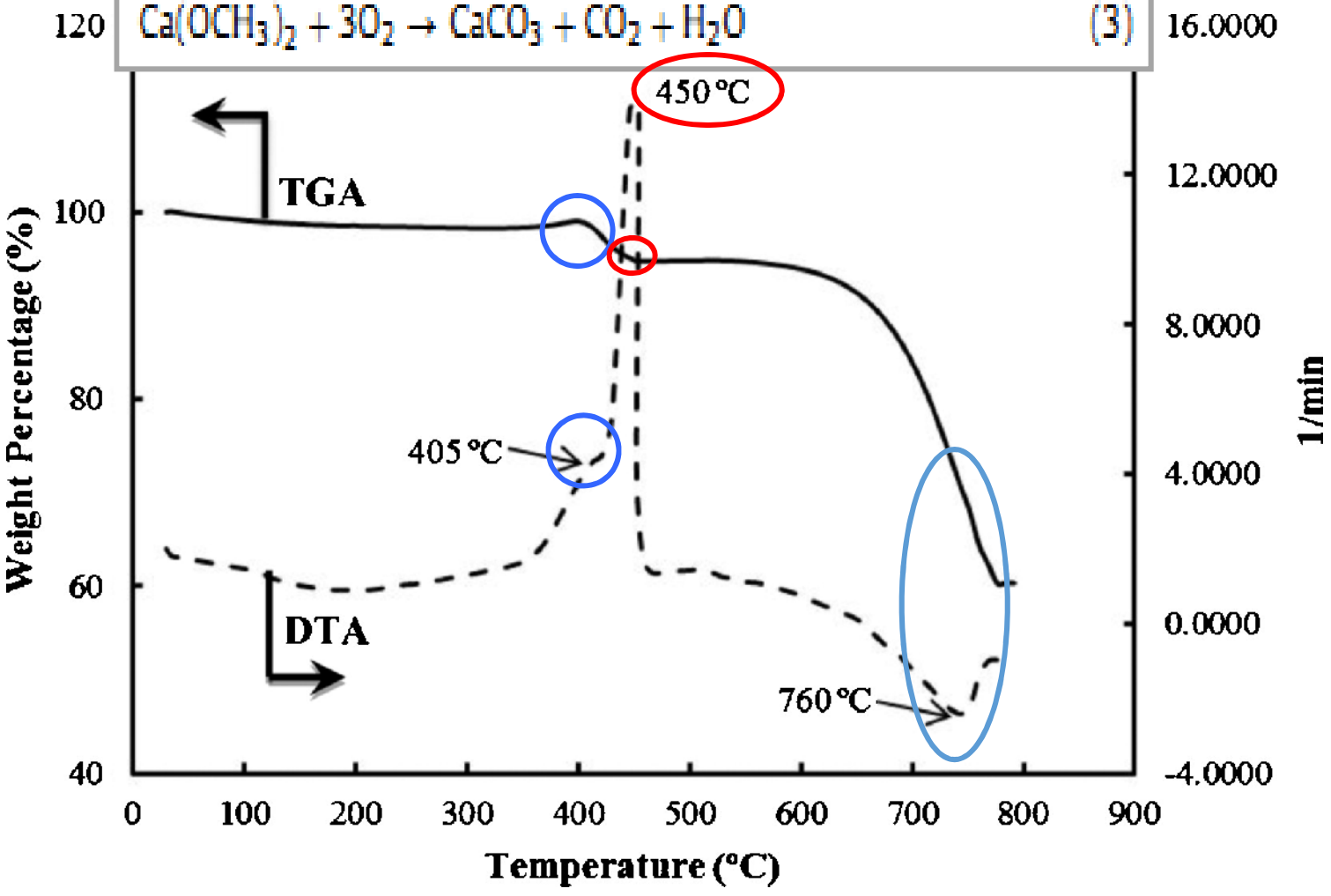
= 1200 Å

B = (98.3 - 98.2)*π/180 = 0.00174

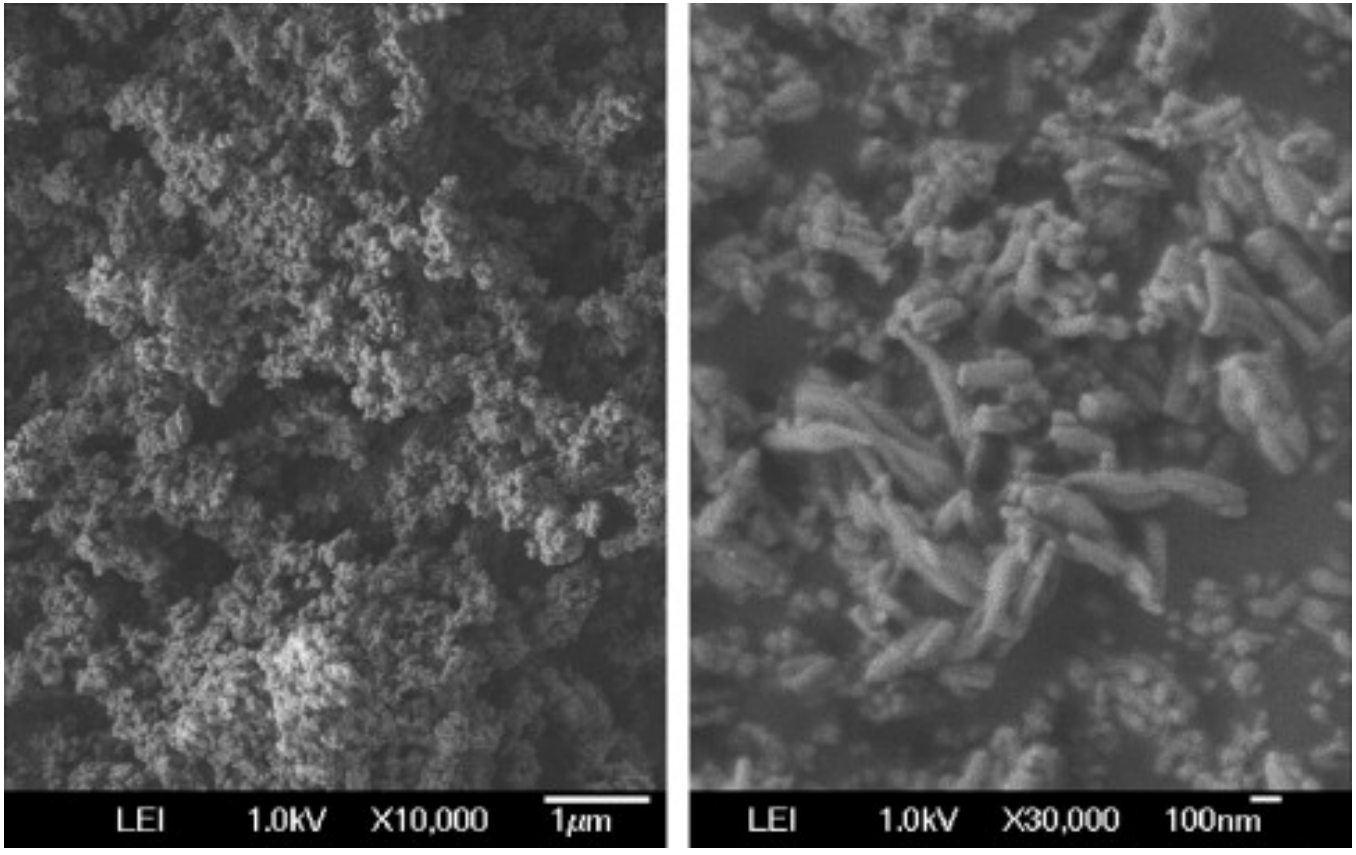
Simple Right!

Characterizations of the synthesized catalyst

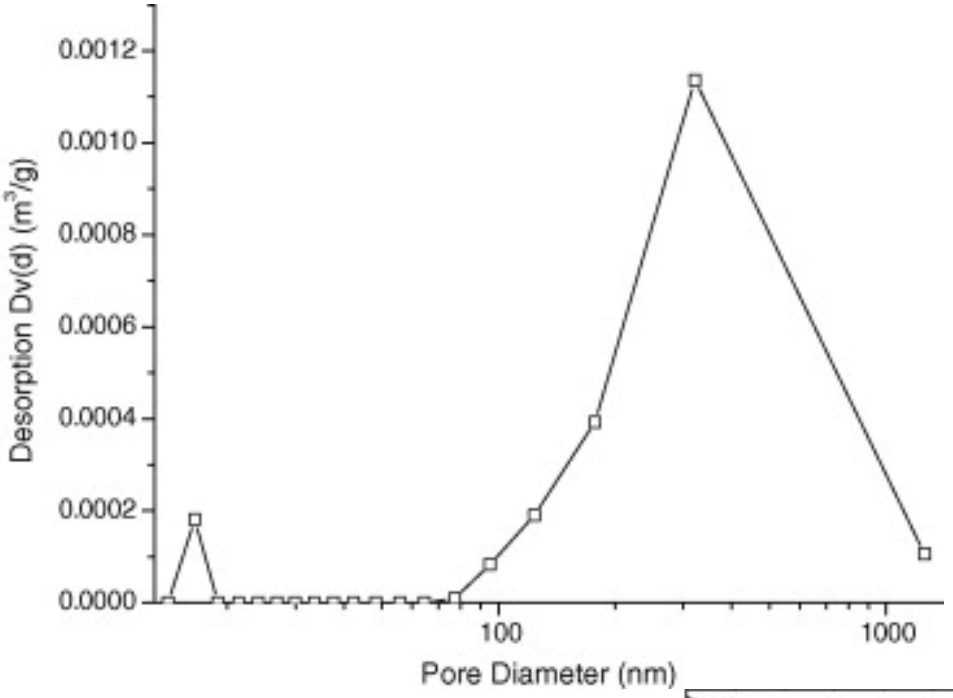
$$Ca(OCH_3)_2 + 3O_2 \rightarrow CaCO_3 + CO_2 + H_2O \quad (3)$$

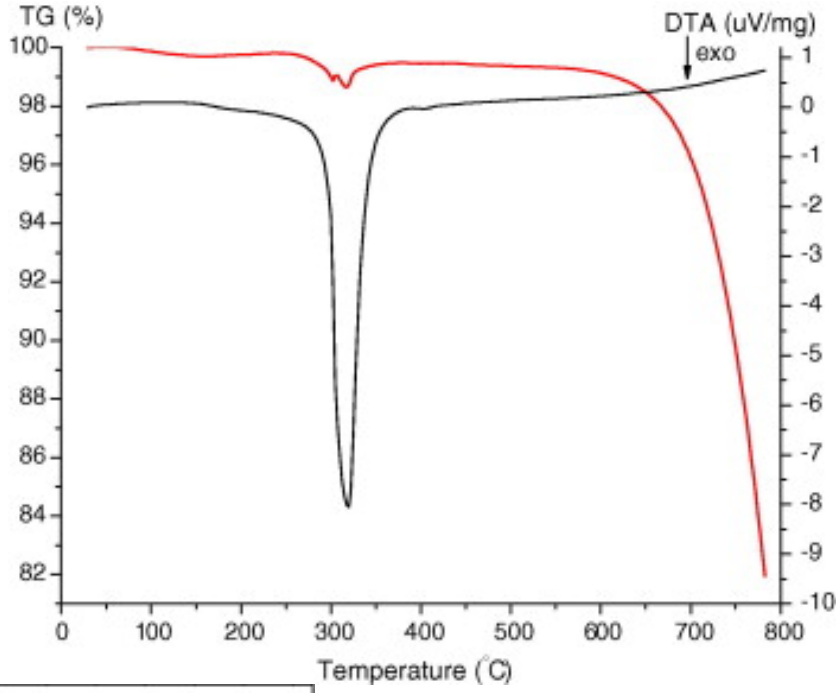


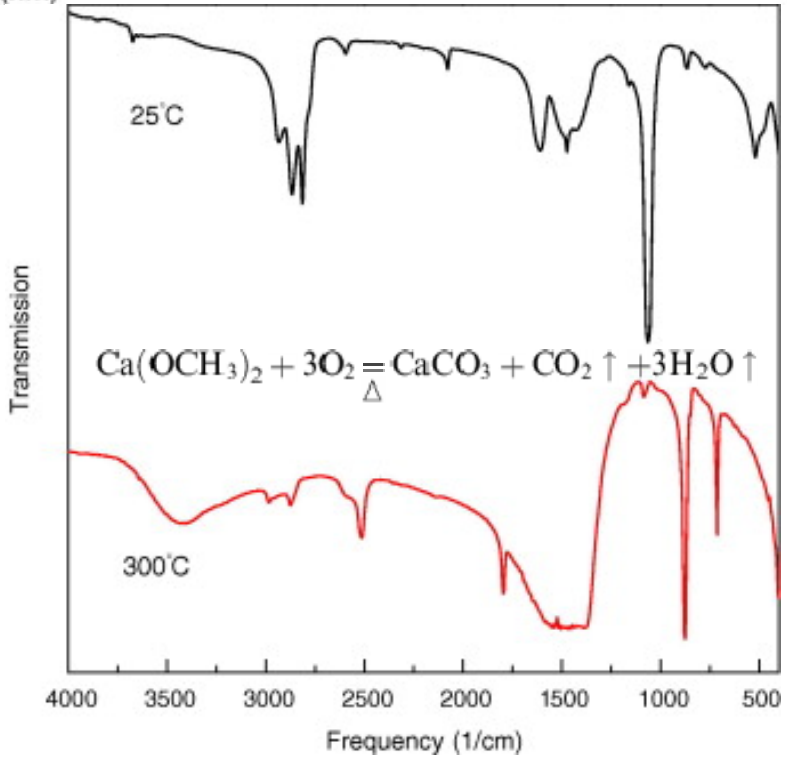
7. TG–DTA thermogram of calcium methoxide.

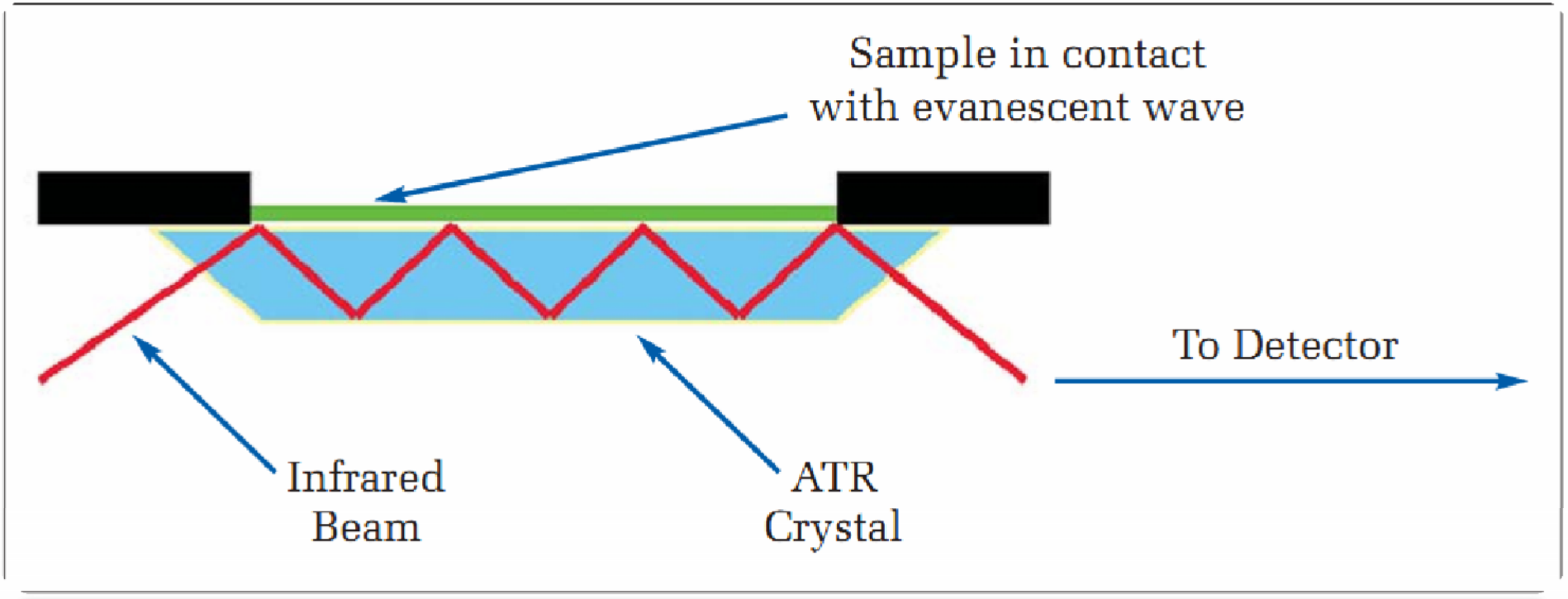


$$Ca + 2CH_3OH \overset{338k}{=} Ca(OH_3)_2 + H_2\uparrow$$


Desorption Dv(d) (m³/g)
0.0012
0.0010
0.0008
0.0006
0.0004
0.0002
0.0000
100
1000
Pore Diameter (nm)

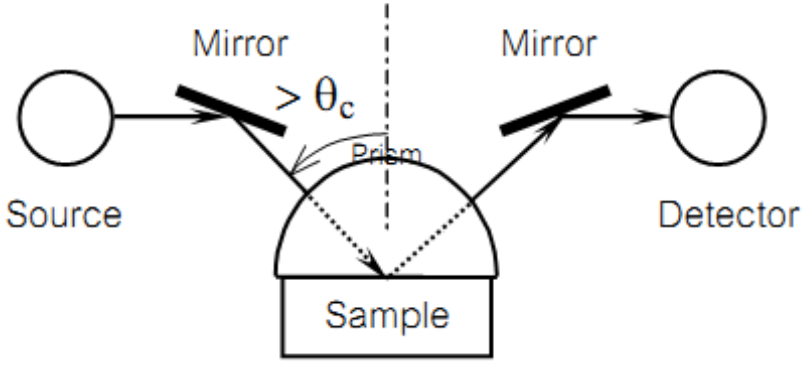

TG (%)
DTA (uV/mg)
exo
100
98
96
94
92
90
88
86
84
82
1
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
0
100
200
300
400
500
600
700
800
Temperature (°C)


25°C
$Ca(OCH_3)_2 + 3O_2 \xrightarrow{\triangle} CaCO_3 + CO_2\uparrow + 3H_2O\uparrow$
300°C
Transmission
4000
3500
3000
2500
2000
1500
1000
500
Frequency (1/cm)


Sample in contact
with evanescent wave
To Detector
Infrared
Beam
ATR
Crystal

ttenuated total reflection (ATR)

Sampling technique ที่สี่เป็นเทคนิคที่มีประสิทธิภาพใน
ารให้ข้อมูลเชิงพื้นผิว หรือข้อมูลที่มีการเปลี่ยนแปลงไป
ามความลึก (Depth dependent property) ได้เป็นอย่างดี
ทคนิคดังกล่าวคือเทคนิค Attenuated total reflection
ATR) เทคนิค ATR อาศัยหลักการของ Internal reflection
ล่าวคือแสงอินฟราเรดจะเดินทางจากตัวกลางที่มีค่าดัชนี
ักเหแสงสูงกว่า (ATR prism) มาตกกระทบที่บริเวณ
อยต่อระหว่าง ATR prism กับตัวอย่างซึ่งมีค่าดัชนีหักเห
สงต่ำกว่าด้วยมุมตกกระทบที่มากกว่ามุมวิกฤต (θ_c) ดัง
าพ



เนื่องจากในเทคนิค ATR นั้น แสงอินฟราเรดไม่ได้
ผ่านตัวอย่าง แต่จะเกิดการสะท้อนกลับที่บริเวณผิว
ของตัวอย่างซึ่งทำให้เกิดสนามไฟฟ้าขึ้นที่บริเวณดังก
สนามไฟฟ้านี้จะ Penetrate เข้าไปในตัวอย่าง โดยความ
ของสนามไฟฟ้าจะมากสุดที่บริเวณผิวหน้าของตัวอ
และลดลงแบบ Exponential ไปตามความลึกจนกระทั่ง
ศูนย์ในที่สุด ซึ่งความลึกที่สนามไฟฟ้าลดลงจนเป็น
นั้นเพียงแค่ประมาณ 1-2 ไมโครเมตรจากผิวหน้า
ตัวอย่างเท่านั้น ดังนั้นข้อมูลที่ได้จากเทคนิค ATR จึง
ข้อมูลเชิงพื้นผิวของตัวอย่าง เทคนิค ATR สาม
ประยุกต์ใช้ได้กับตัวอย่างทั้งที่เป็นของเหลวและของ
อย่างไรก็ตามเนื่องจากเทคนิค ATR เป็นเทคนิคที่ต้อง
การสัมผัสกันระหว่าง ATR prism กับตัวอย่างและคุณ
ของสเปกตรัมที่ได้จะขึ้นอยู่กับคุณภาพของการสั
ดังกล่าวโดยตรง ดังนั้นสำหรับตัวอย่างที่สามารถสัมผั
Prism ได้ดีเช่นของเหลว Paste หรือของแข็งที่นุ่ม
ยืดหยุ่นได้นั้นสามารถทำการวิเคราะห์ได้ทันที แต่ถ้า
เป็นของแข็งที่ผิวหน้าไม่เรียบจำเป็นจะต้องเตรียมตัว
ให้มีผิวหน้าเรียบก่อนจึงจะทำการวิเคราะห์ด้วยเท
ATR ได้