

# The Conversion of Biomass to Biofuels



**Professor (Em.) Aharon Gedanken**  
**Department of Chemistry, Bar-Ilan University, Ramat-Gan**  
**Israel**

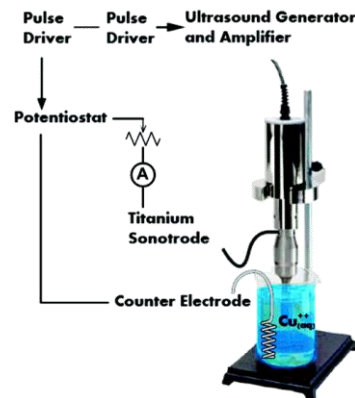
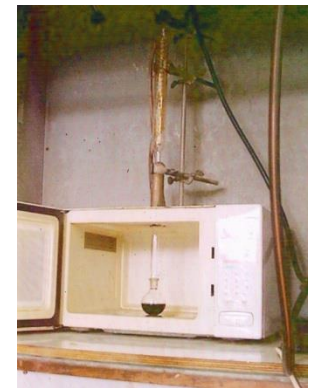
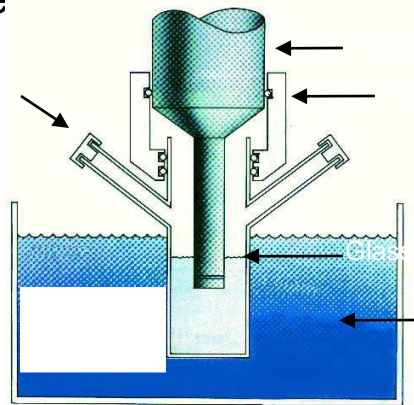
**Lecture at Jerusalem**

**22<sup>nd</sup> October, 2013**

# Novel methods for the fabrication of nanomaterials

Gedaken's laboratory has fabricated a large variety of nanoparticles using 4 techniques

- 1) Sonochemistry,
- 2) Microwave radiation,
- 3) Sonoelctrochemistry, and
- 4) RAPET (Reactions under Autogenic Pressure at Elevated Temperatures)



---

# Alternate Energy Sources

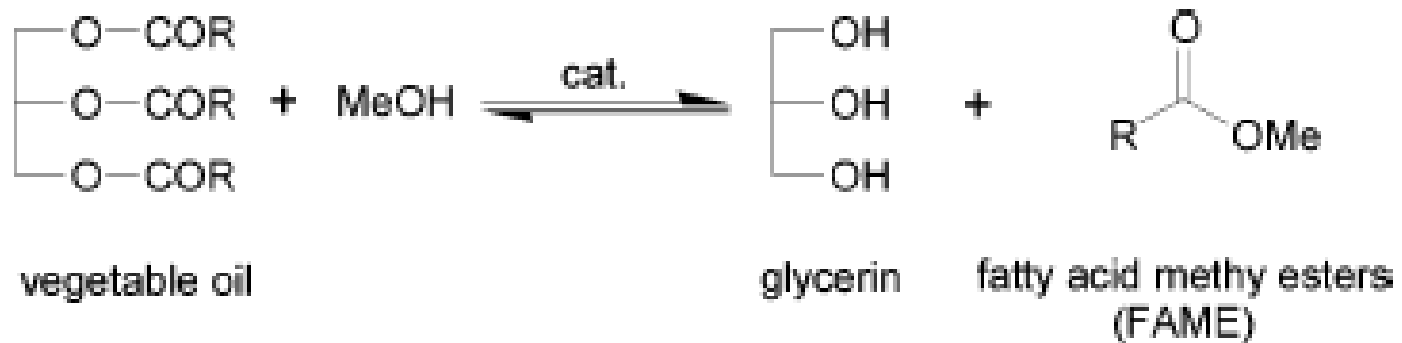
## Why alternate fuels?

- Depleting fossil fuels
- Non-uniform global distribution of fossil fuels
- Growing population
- Increasing demand for transportation fuel
- CO<sub>2</sub> emissions

## Why bioethanol?

- Tested transportation fuel
- Carbon neutral
- Renewable and Sustainable
- Agricultural waste (cellulose) as a precursor

# Preparation of Biodiesel

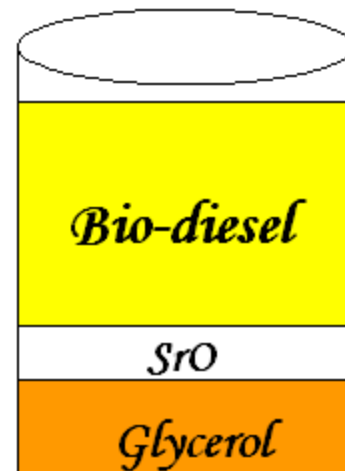


- *Biodiesel is made from vegetable oils or animal fats by transesterification with methanol using an acid or base catalyst.*
- *The most commonly used catalysts in transesterification reaction are: NaOH , KOH , H<sub>2</sub>SO<sub>4</sub>.*

## **:Optimization of Bio-Diesel Production**

**Probing the New Combination of the Microwave**

**.Irradiation of Cooked Oil and SrO as a Solid Catalyst**



*,Microwave Irradiation of a Reaction Mixture of SrO, Methanol  
and Oil leads to Creation of 3 Phases*

## Optimum Result:

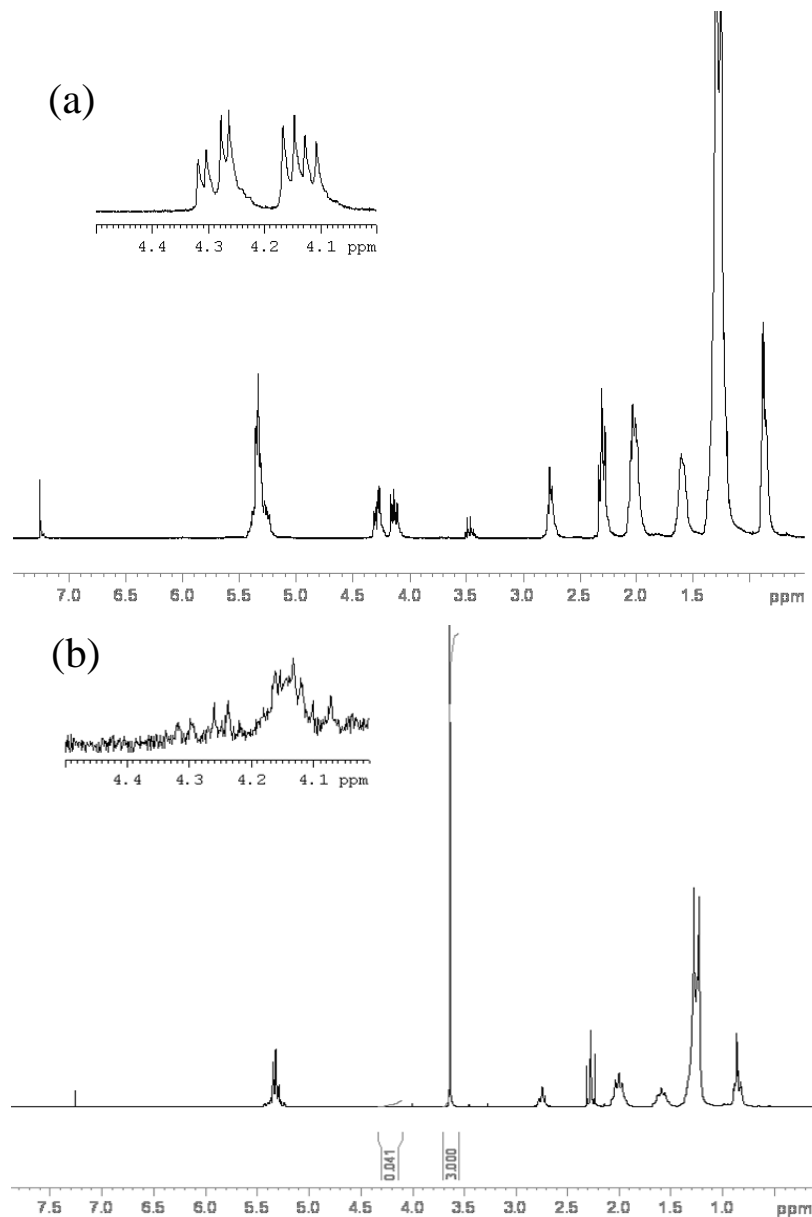
- 99% conversion in 40 seconds unstirred microwave irradiation with SrO, or in **10 seconds** while stirring.

Amounts: Oil / Methanol / SrO

15 gr / 4.05 ml / 0.276 gr

- Using KOH under the same conditions leads to 83% conversion!

- (a)  $^1\text{H}$ NMR spectrum of wastes of cooked oil. (b)  $^1\text{H}$ NMR spectrum of bio-diesel production from wastes of cooked oil obtained after 40 sec unstirred, or **10 seconds** for the stirred reaction using SrO as a catalyst.

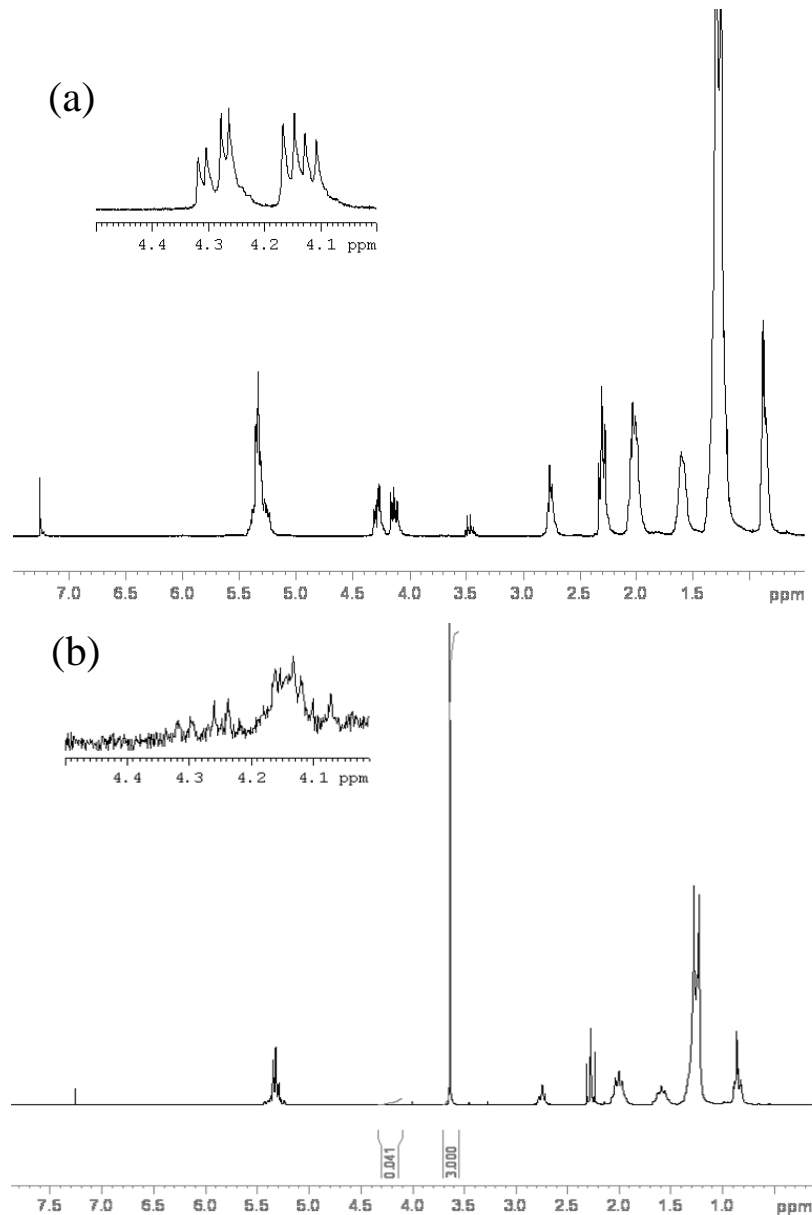


## Optimum Result:

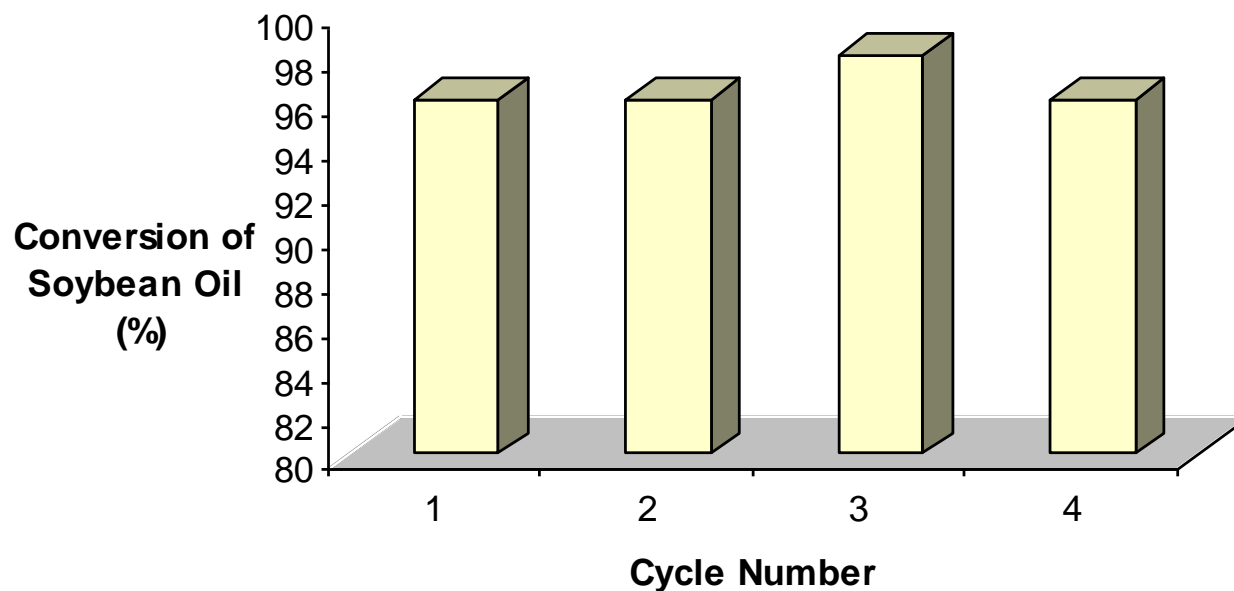
99% conversion in 40 seconds of  
microwave irradiation with SrO.  
Amounts: Oil / Methanol / SrO  
15 gr / 4.05 ml / 0.276 gr

Using KOH under the same  
conditions leads to 83%  
conversion!

(a)  $^1\text{H}$ NMR spectrum of wastes of  
cooked oil. (b)  $^1\text{H}$ NMR spectrum  
of bio-diesel production from  
wastes of cooked oil obtained  
after 40 sec using SrO as a  
catalyst.



## Repeated Activity of the Catalyst



*The result confirm the stability and the sustained activity of SrO, which is of great importance for industrial application*



- 
- In the next stage we have investigated the bio-diesel production directly from the microalgae biomass of *Nannochloropsis* by microwave and ultrasound radiation

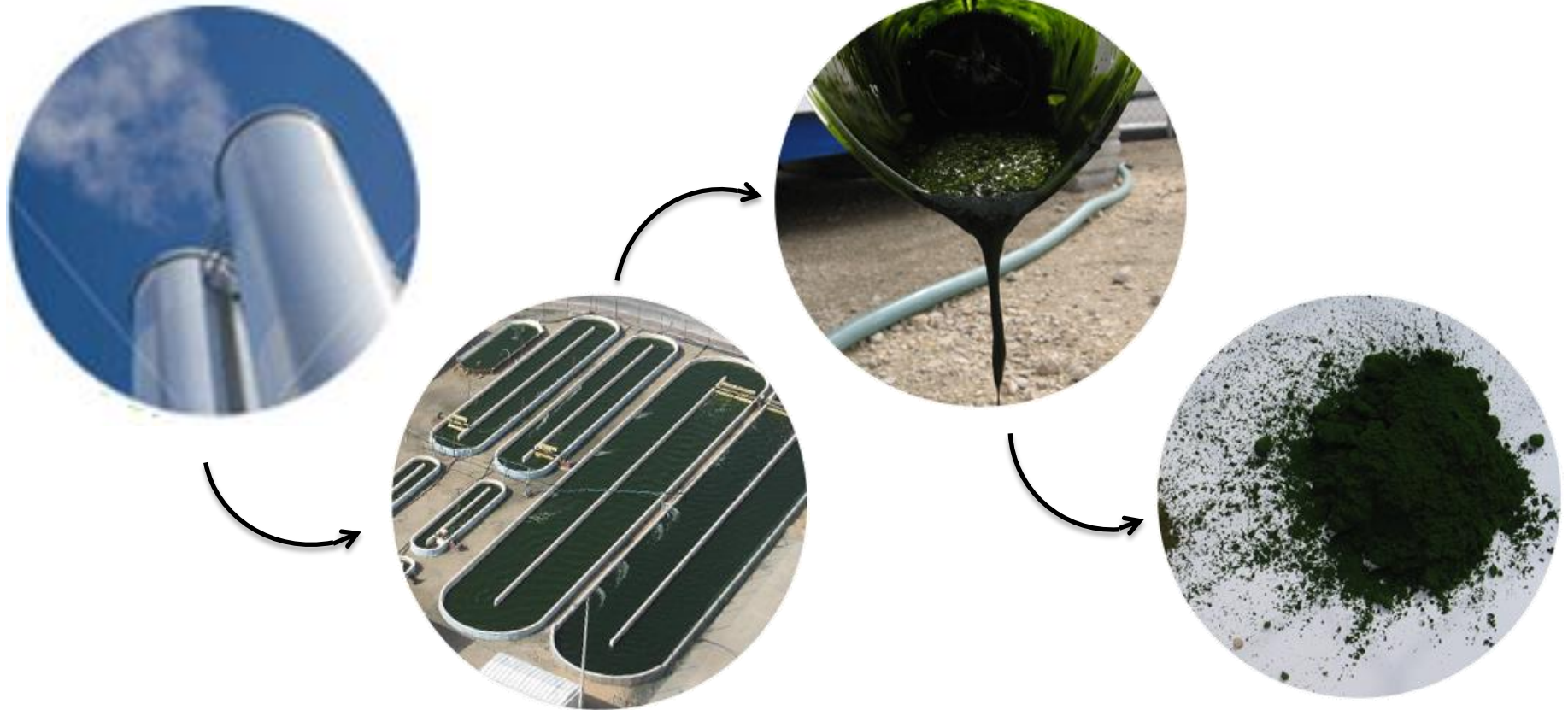
# How were the microalgae prepared?

- **The microalgae was provided to us by Seambiotic.** This company grows the algae on seawater. The cultures were supplied with N & P and C inorganic nutrients, where the C was supplied by coal burning scrubbed flue gas containing 13% CO<sub>2</sub>. A culture of the marine Eustigmatophyte *Nannochloropsis sp.* was inoculated in outdoor raceway ponds at a concentration of less than 0.25 g/L, grown for 7 days to a concentration of 0.5 g/L. The culture was harvested using a continuous centrifuge (GEA Westfalia) and the paste was dried with a spray dryer (Anhydro) to obtain a dry powder.

## Seamiotic microalgae ponds



# Seamiotic microalgae cultivation process



Culture Inoculation at  
concentration of 0.25 g/L  
(Raceway Pond)

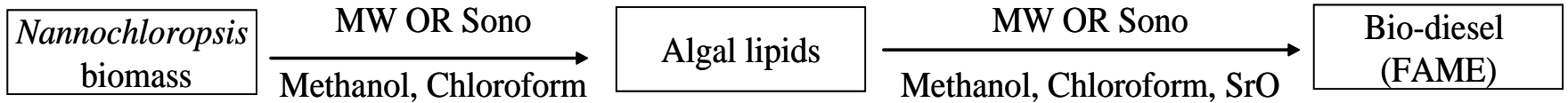
Culture concentration  
increase to 0.5 g/L

Harvest  
Paste at concentration of 150-200 g/L  
(Continuous centrifuge)

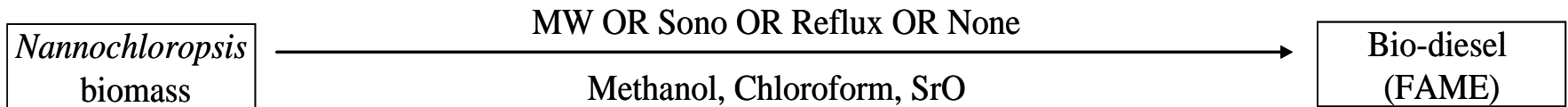
Drying  
Dry algae powder  
(Spray drier)

# Bio-diesel production from the microalgae biomass of *Nannochloropsis*

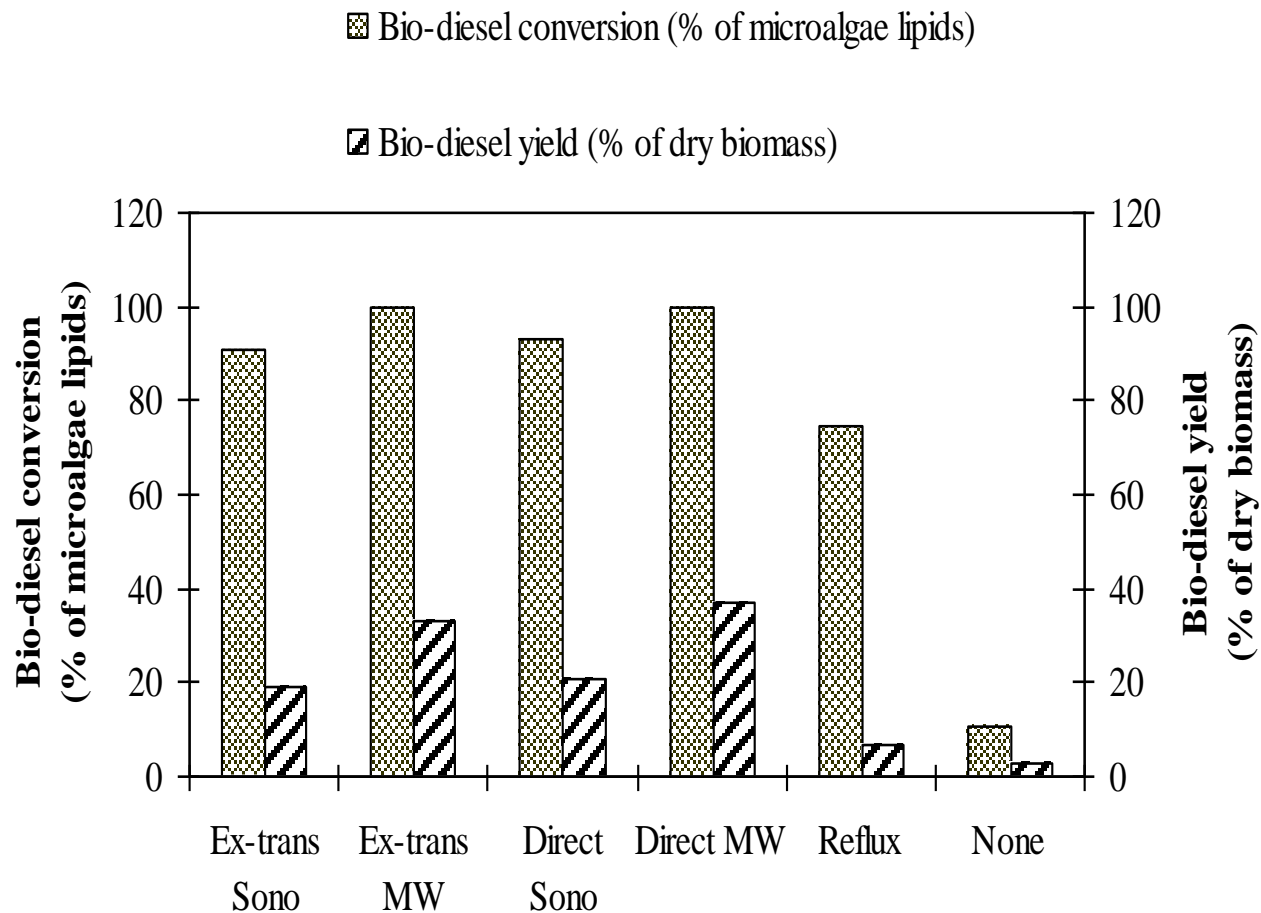
(a) A two-step reaction, namely, extraction and transesterification:



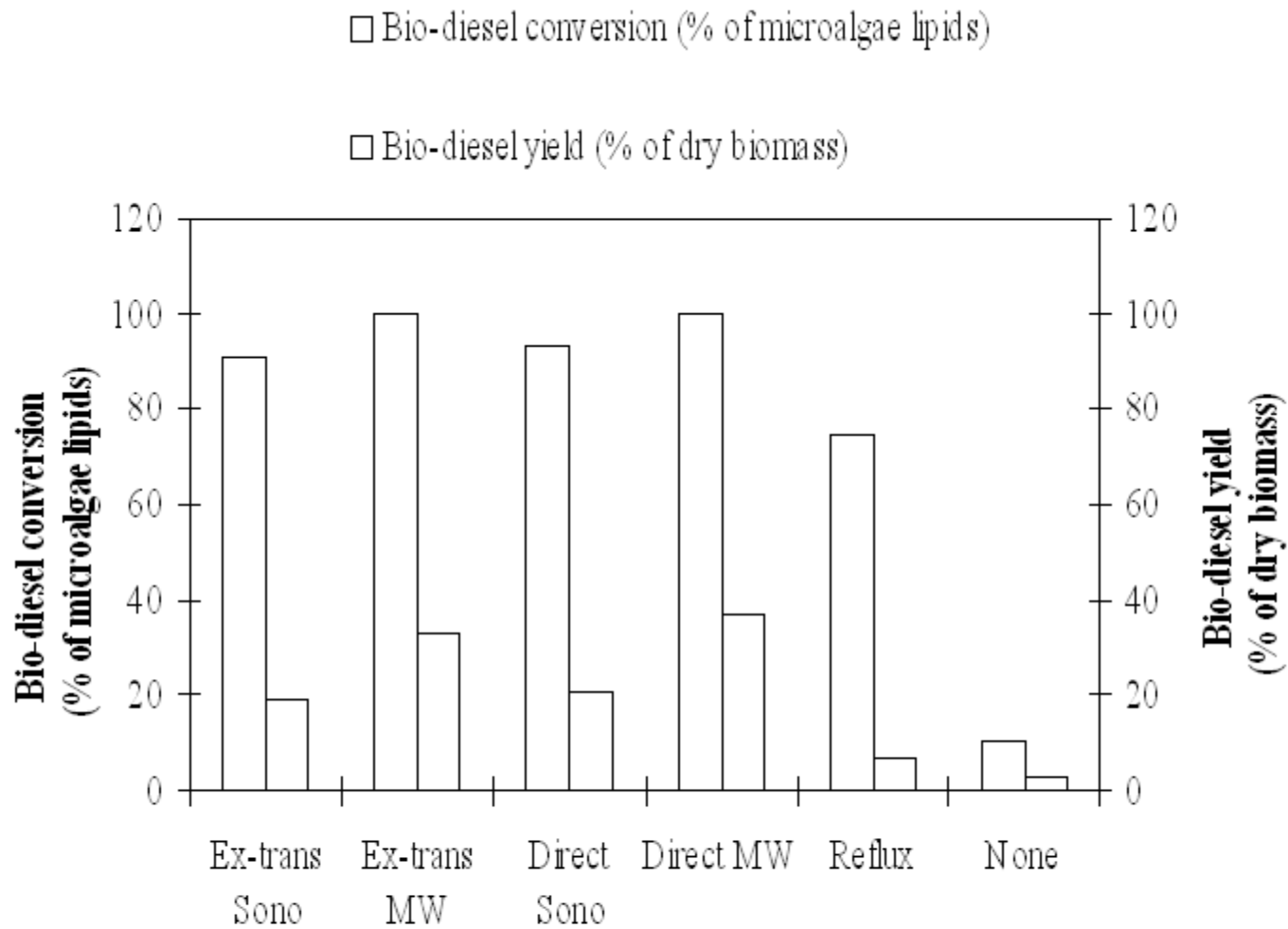
(b) A one-step direct transesterification



Direct transesterification reaction using microwave resulted the highest bio-diesel yield of **37.1%** with a conversion (**99.9%** conversion) of the triglyceride to bio-diesel.



Bio-diesel yield of the *Nannochloropsis* microalgae and bio-diesel conversion of the microalgae lipids using various techniques. Five techniques used in bio-diesel production: (Ex-trans Sono) extraction and transesterification reaction steps occurred separately using sonication, (Ex-trans MW) extraction and transesterification reaction steps occurred separately using microwave, (Direct Sono) direct transesterification without the initial extraction step using sonication, (Direct MW) direct transesterification without the initial extraction step using microwave, (Reflux) direct transesterification without the initial extraction step using regular reflux technique, and (None) extraction and transesterification reaction occurred without heating and stirring.



Bio-diesel yield of the *Nannochloropsis* microalgae and bio-diesel conversion of the microalgae lipids using various techniques. Five techniques used in bio-diesel production: (Ex-trans Sono) extraction and transesterification reaction steps occurred separately using sonication, (Ex-trans MW) extraction and transesterification reaction steps occurred separately using microwave, (Direct Sono) direct transesterification without the initial extraction step using sonication, (Direct MW) direct transesterification without the initial extraction step using microwave, (Reflux) direct transesterification without the initial extraction step using regular reflux technique, and (None) extraction and transesterification reaction occurred without heating and stirring.

# Direct transesterification of jatropha seeds for bio-diesel production by microwave and SrO catalyst



***Direct transesterification reaction using microwave resulted bio-diesel yield of 41.08% with a conversion (99.71% conversion) of the triglyceride to bio-diesel.***

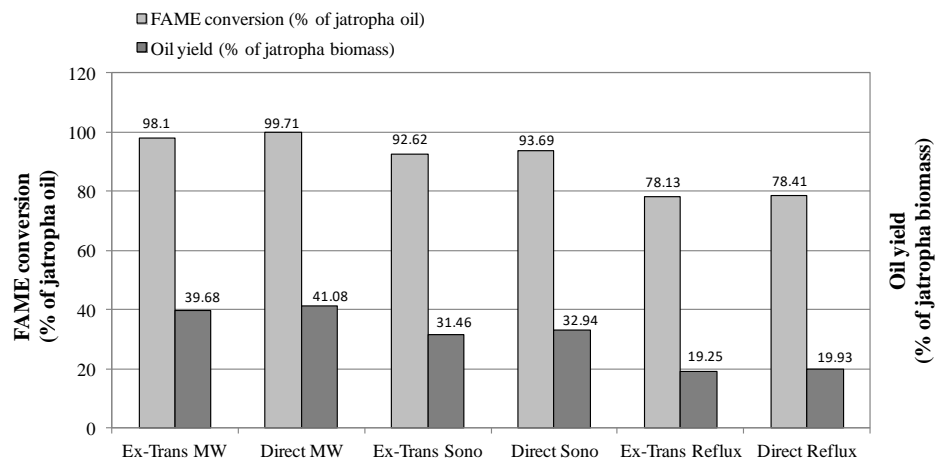
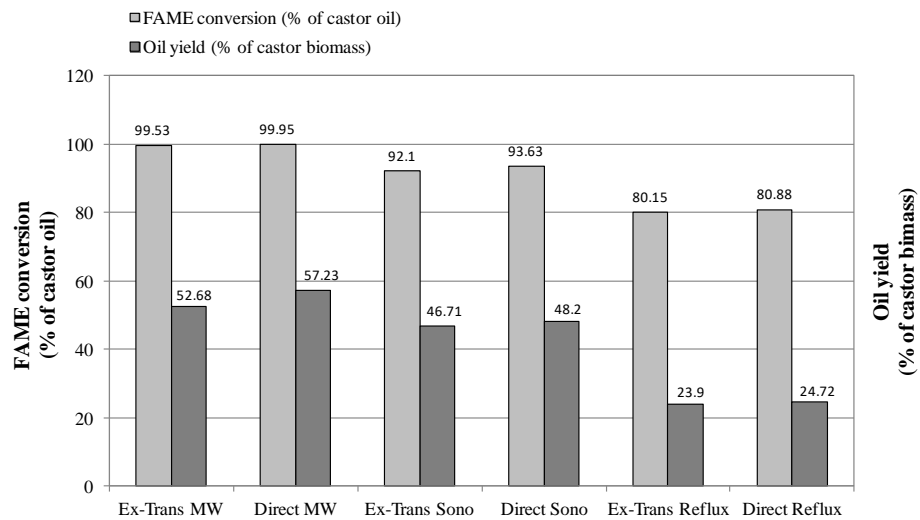
1/21/2023



## Direct transesterification of castor seeds for bio-diesel production by microwave and SrO catalyst



Direct transesterification reaction using microwave resulted the highest bio-diesel yield of **57.23%** with a conversion (**99.95%** conversion) of the triglyceride to bio-diesel.



---

## Drive for research in Bioethanol – Cost reduction

World wide focus - bioethanol as a substitute to gasoline ○

Feedstocks for ethanol - Brazil (sugar cane molasses), United States (corn), ○  
India (sugar cane), Thailand (cassava),  
France (sugar beet), China (corn), Canada (wheat)

Brazil in 2010 - 27 billion liters of bioethanol produced from sugar cane juice or molasses

US in 2010 - produced 50 billion liters of bioethanol from corn ○

### Bioethanol Industry

In Brazil - 243 bioethanol processing plants and nearly 33, 620 ethanol service stations ○

In US - 113 ethanol biorefineries in operation with 1073 ethanol stations ○

### Possible ways of reducing bioethanol production costs

Identifying appropriate feedstock ✓

Improving the feed stock pretreatment ✓

Lowering of enzyme dosage or developing a robust chemical hydrolysis process ✓

Improving over all starch and cellulose hydrolysis ✓

Shortening the fermentation time ✓

---

## Advantages of Bioethanol

- Renewable and environmentally friendly and carbon neutral fuel○
- Blended with petrol or used as neat alcohol○
- Higher octane no. and higher heat of vapourisation○

## Why Cellulose for ethanol?

- No food to fuel conflict➤
- Most common carbohydrate➤
- Annual world biosynthesis is  $10^{11}$  t➤
- Most widespread and readily available solid organic waste➤
- 1/3<sup>rd</sup> of the wt. of all trees, vines, grasses and straws comprise of cellulose➤
- Renewable and replenished by photosynthesis and growth➤
- Vast potential feed stock to chemical industry➤



**Scheme 1.** Schematic representation of the formation of ethanol from biomass

***Hydrolysis of cellulose and fermentation of sugars are the two important reactions in the conversion of biomass to fuel ethanol***

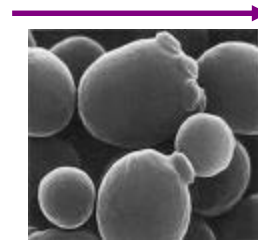
# How to make the fermentation faster?

Use of bathsonicator accelerated the fermentation rate

## Glucose fermentation to ethanol

**Yeast (*Saccharomyces cerevisiae*)**

**Sugars  
(D-glucose, D-sucrose)**



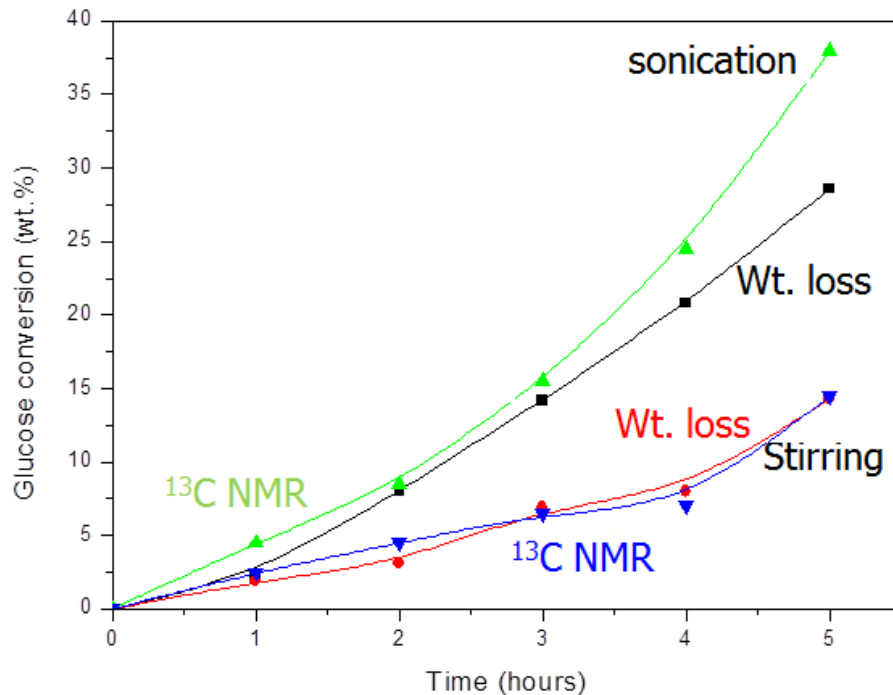
**Ethanol**

Theoretical yield of ethanol:

1 g glucose yields 0.51 g ethanol  
1 g sucrose yields 0.54 g ethanol

**Yeast strain employed: Bakers yeast (Bravo brand)**

# Acceleration of Fermentation of Glucose at 30 °C



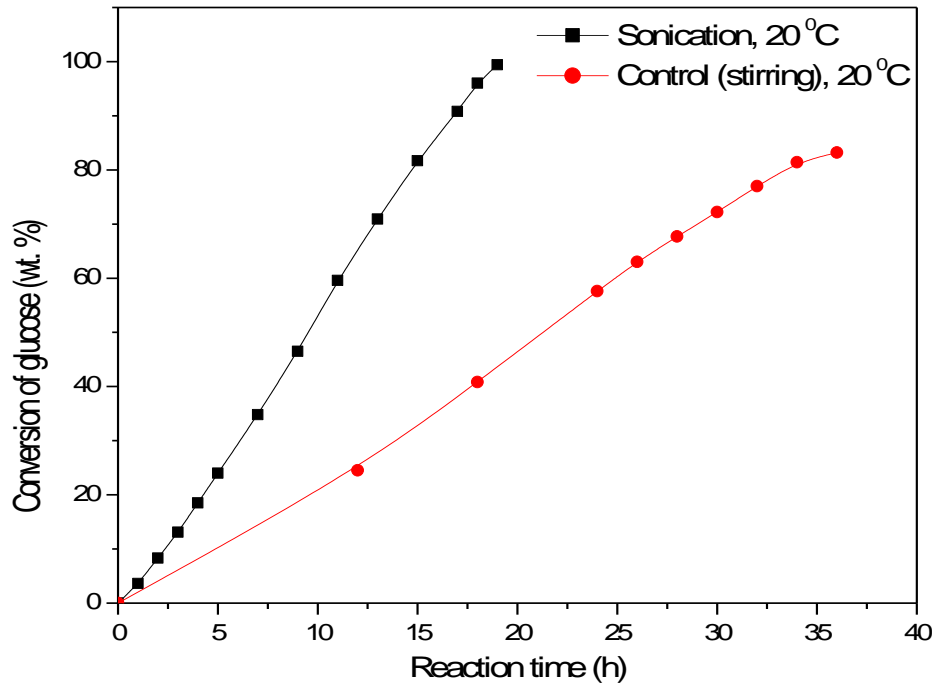
❖ Glucose conc. = 20 %

❖ sonication: 38% conversion in 5 h  
Stirring: only 14.5 % conversion in 5 h

❖  $k_{\text{sonication}} = 15.35 \times 10^{-6} \text{ sec}^{-1}$   
 $k_{\text{stirring}} = 6.67 \times 10^{-6} \text{ sec}^{-1}$

**Kinetics from  $^{13}\text{C}$  NMR and from wt. loss**

# Acceleration of Fermentation of Glucose at 20 °C



❖ Glucose conc. = 20 %

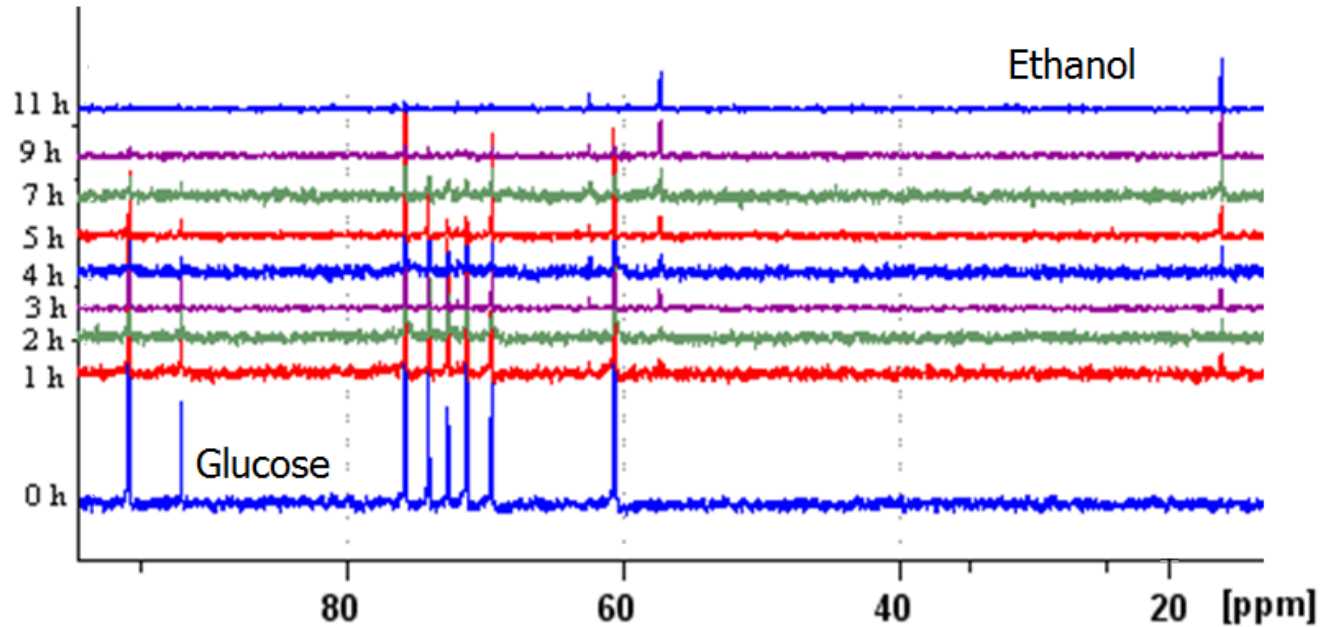
❖ Sonication: 100%  
conversion in 19 h  
Stirring: 36 h is required for  
the complete conversion

$$k_{\text{sonication}}: 6.31 \times 10^{-6} \text{ sec}^{-1}$$
$$k_{\text{stirring}}: 2.465 \times 10^{-6} \text{ sec}^{-1}$$

**Kinetics from wt. loss of the broth**

# Complete glucose fermentation under sonication at 30 °C

Glucose conc. – 20 %

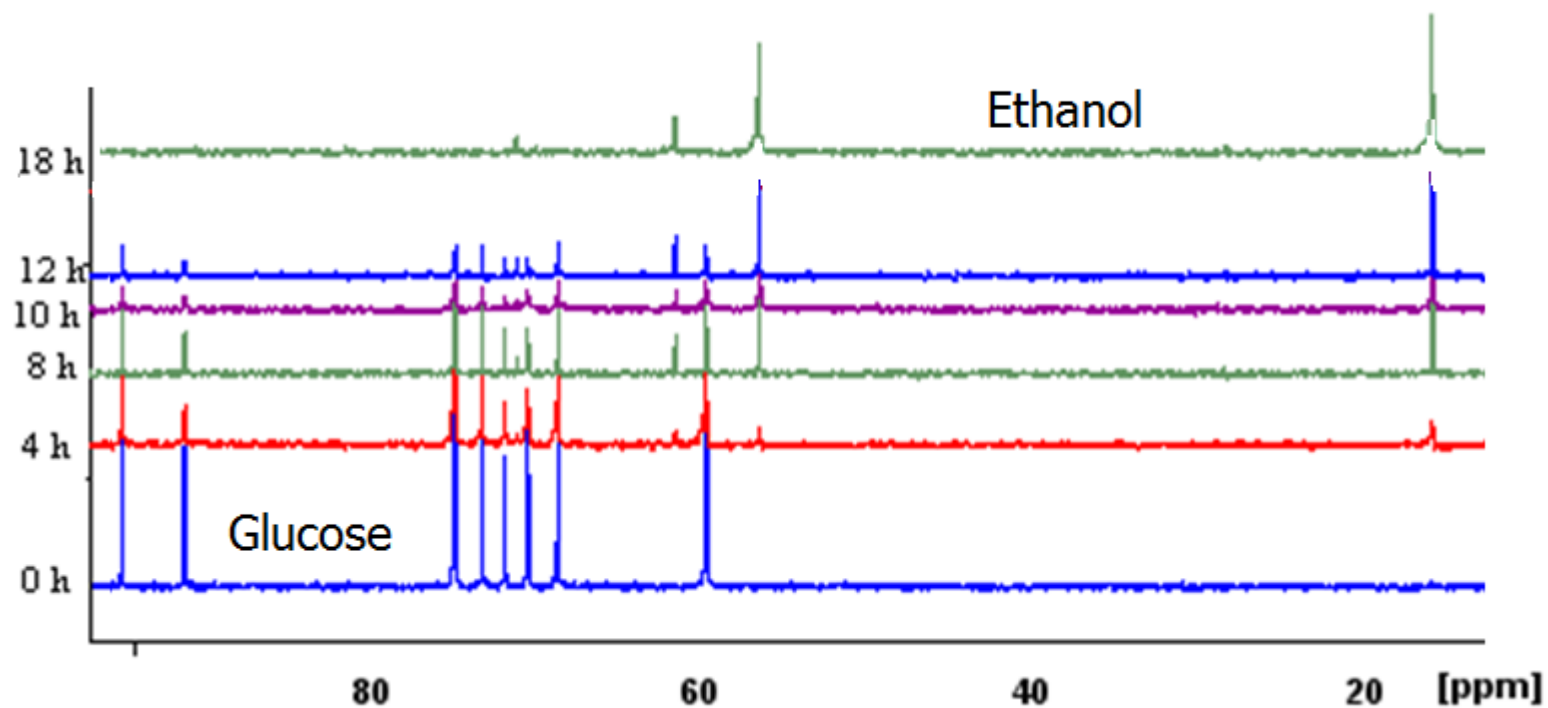


$^{13}\text{C}$  NMR spectra (from 0 to 11 h)

- With time intensity of the peaks corresponding to ethanol increased and the intensity of peaks corresponding to glucose decreased
- Complete conversion of glucose to ethanol in 11 h



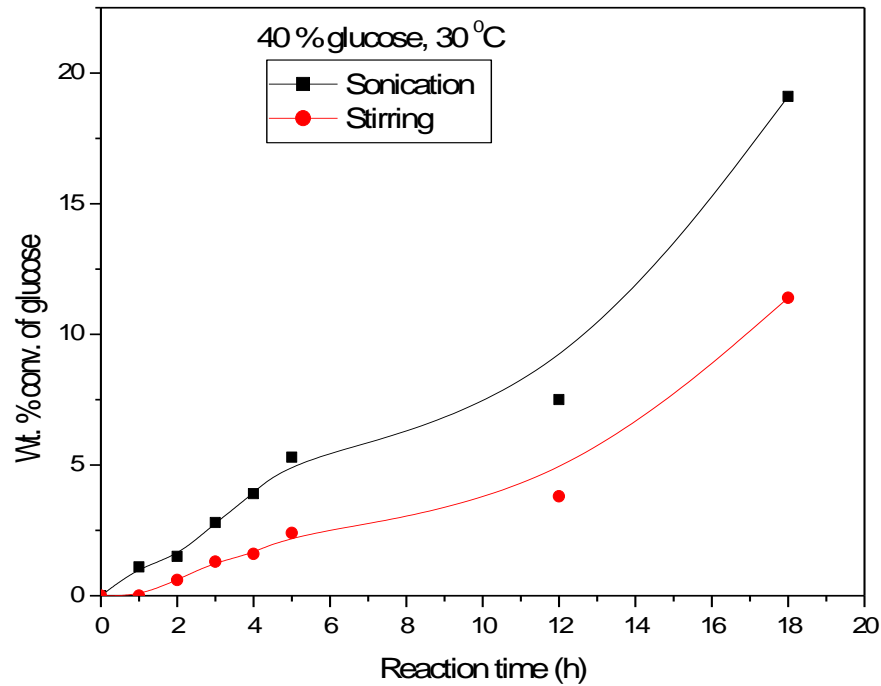
## Complete glucose fermentation under stirring at 30 °C



$^{13}\text{C}$  NMR spectra (from 0 to 18 h)

- Complete conversion of glucose to ethanol 18 h with stirring relative to 11 h under sonication

# Acceleration of fermentation even at 40 % glucose concentration

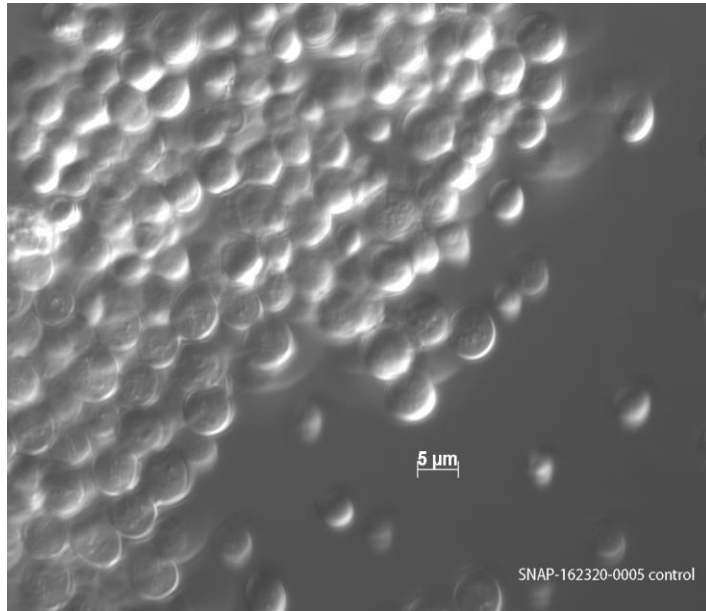


## Glucose conversion with sonication Vs stirring

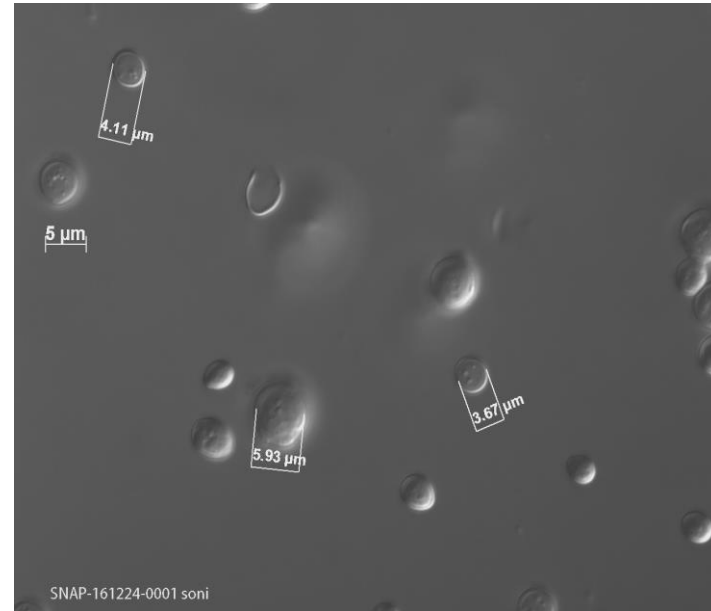
Sonication: 19 % conversion in 18 h

Stirring: 11 % conversion in 18 h

# How does yeast cells appear? – Sonication Vs Stirring



Aggregates of yeast cells  
Stirring



Dispersed yeast cells  
Sonication

Sonication facilitated dispersion of yeast aggregates

The yeast is reusable even after sonication

What are the other avenues for faster production of bioethanol?

---

# Accelerated production of bioethanol using ultraturrax

## Research Goals:

- 1) To develop a process to convert glucose to ethanol at accelerated rates.
  - 2) To evaluate the viability of various feedstocks for bioethanol production (glucose, sucrose, molassa, dates syrup).
  - 3) To identify additives that contribute to accelerating fermentation reaction.
  - 4) To optimize the fermentation conditions (temperature, pH, shelf life of yeast).
-

## Fermentation with Ultraturrax

Fermentation – with *Saccharomyces cerevisiae*

Sugar sources – D-Glucose, Sucrose, Molassa

Fermentation broth – yeast + sugar + water

Sugar/yeast ratio – 10

Temperature – 30 °C

Fermentation using ultraturrax – 5,000, 10,000 and 20,000 rpm

Fermentation in incubator – 0 rpm

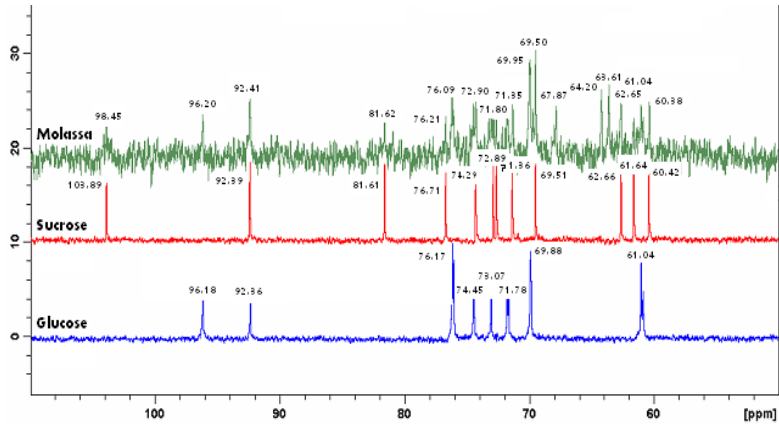
Effect of additives on fermentation – activated carbon

Effect of pH – at 2 and 6

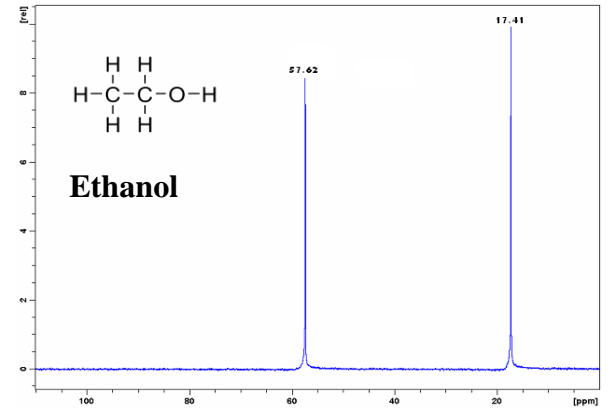
$^{13}\text{C}$  NMR spectroscopy – Kinetics of fermentation



# Bioethanol Production Process



Yeast



Glucose



Sucrose



Molassa

Ultraturrax/  
Incubator

Ethanol NMR



## Does stirring speed affect the fermentation rate?

### Fermentation of glucose

Stirring speed, rpm	Rate constant, k (sec <sup>-1</sup> )
0	2.1 x 10 <sup>-5</sup>
5,000	2.0 x 10 <sup>-5</sup>
10,000	4.0 x 10 <sup>-5</sup>
20,000	4.2 x 10 <sup>-5</sup>

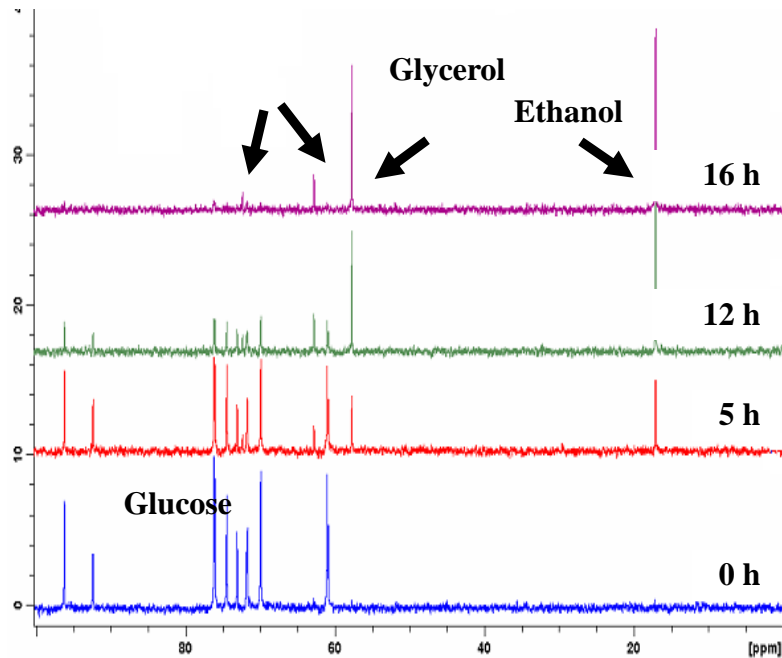
Mechanical agitation accelerated the fermentation rate.

10, 000 rpm is the optimum stirring speed.

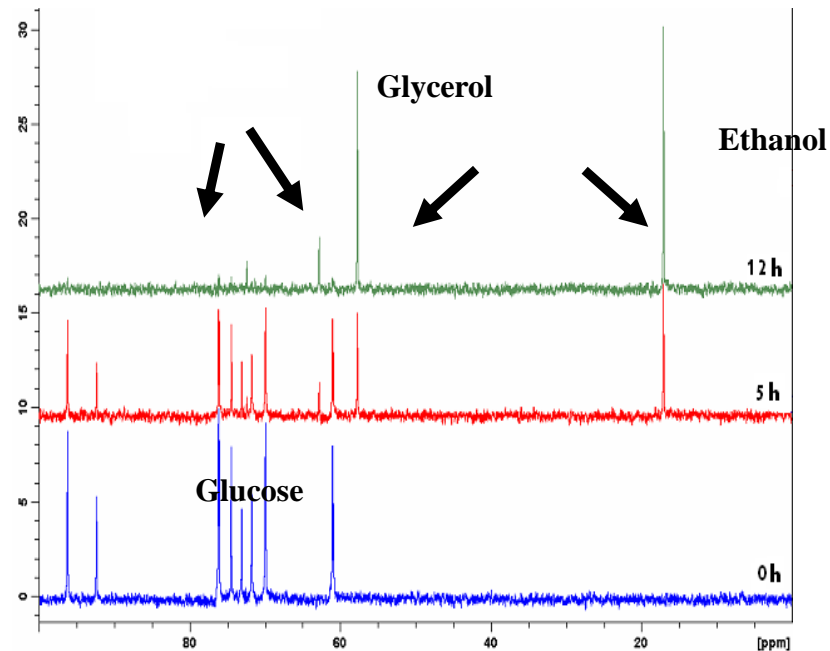
Faster removal of CO<sub>2</sub> from the broth.

# Ultraturrax accelerated glucose fermentation

## Incubation



## Ultraturrax



Method

Reaction rate constant,  
 $k$  ( $\text{sec}^{-1}$ )

Incubation

$2.1 \times 10^{-5}$

Ultraturrax

$4.0 \times 10^{-5}$

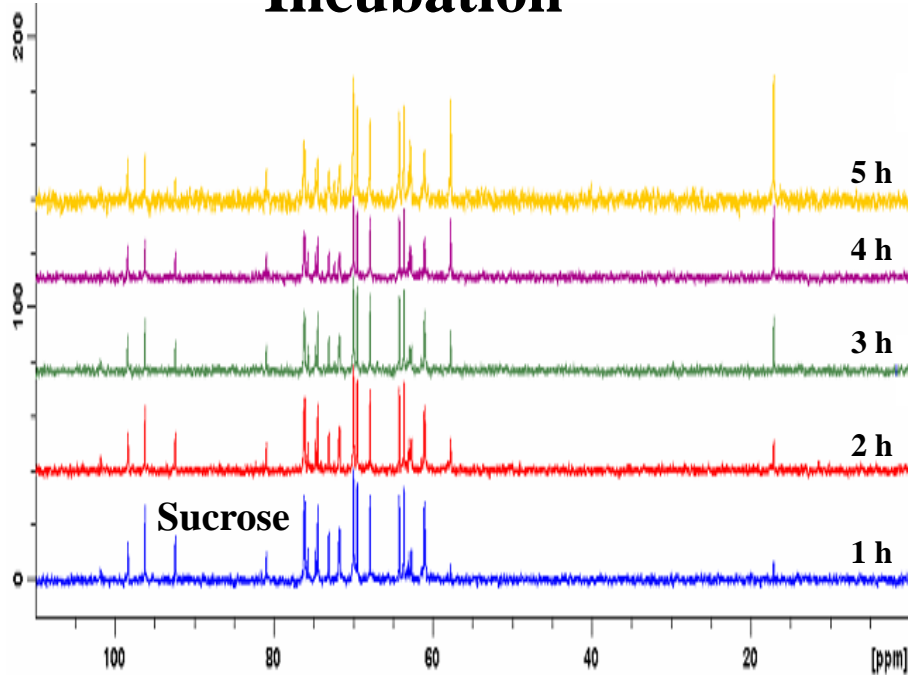
Two fold enhancement in reaction rate by using ultraturrax:

$$k_{\text{ultraturrax}}/k_{\text{incubator}} = 1.9$$

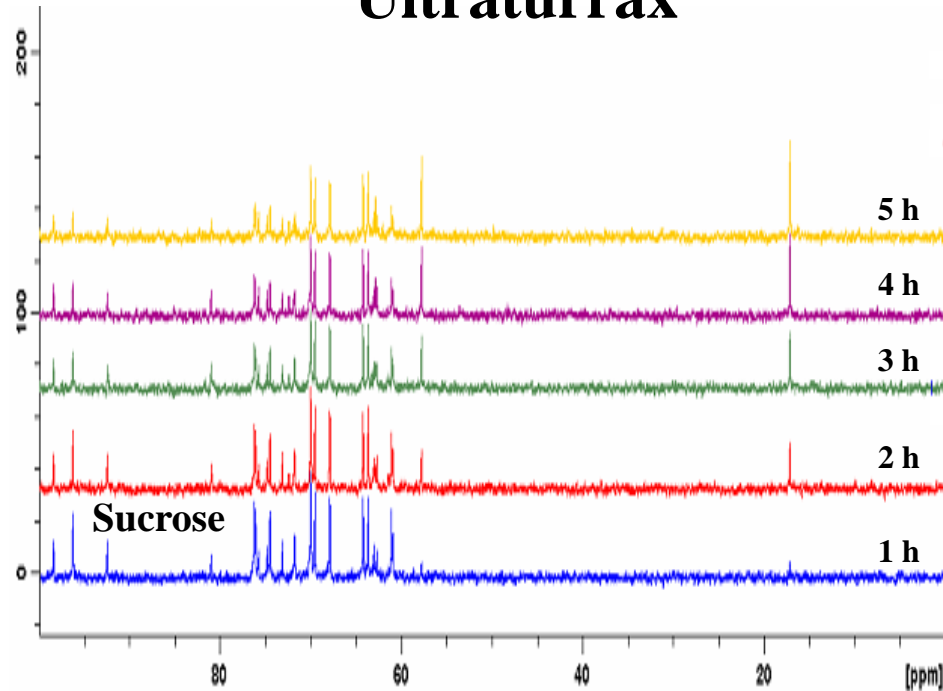


# Sucrose (disaccharide) fermentation

## Incubation



## Ultraturrax

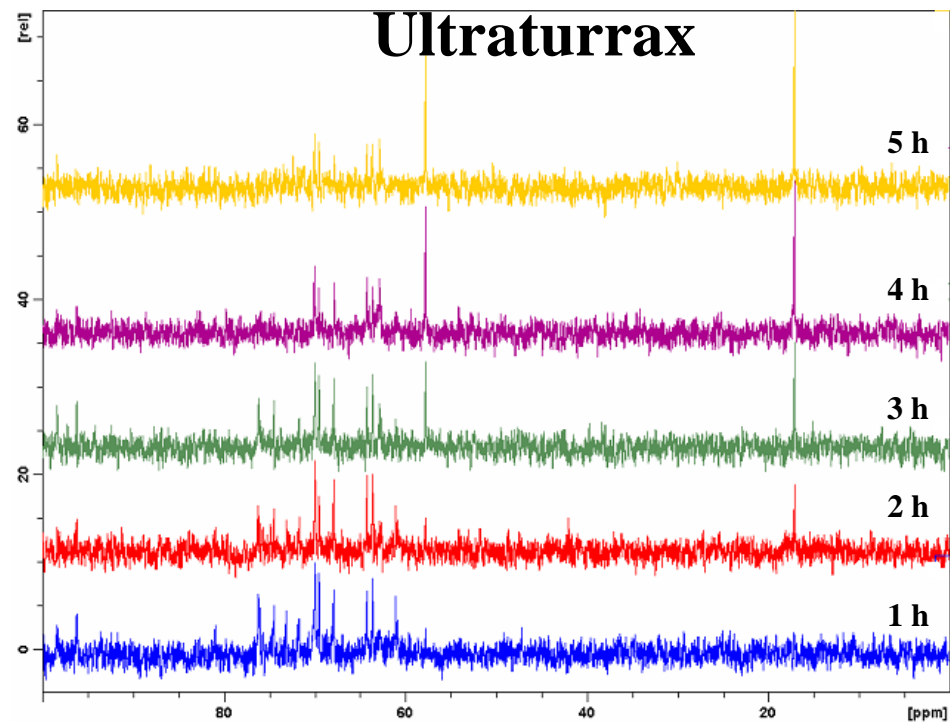
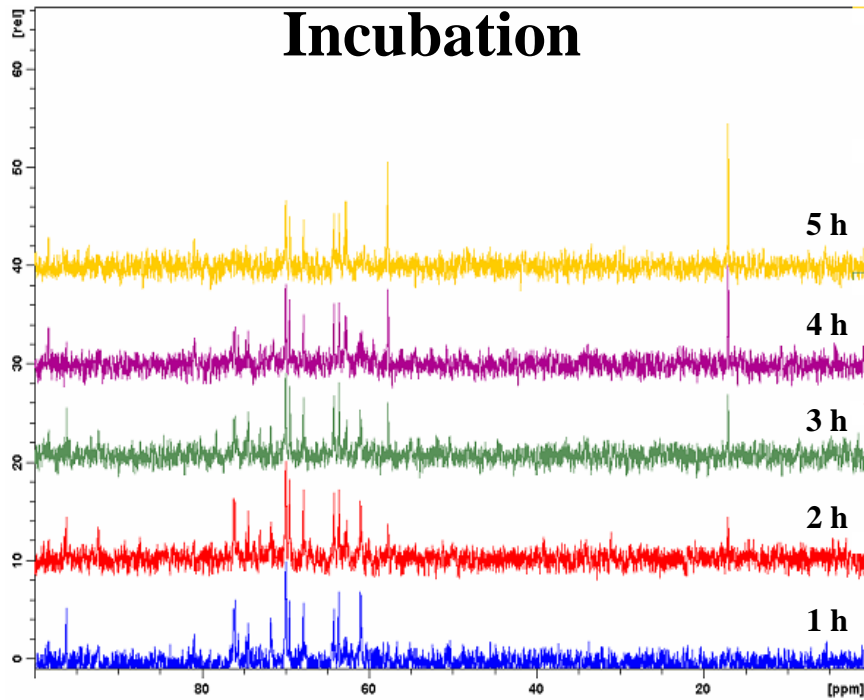


Method	Reaction rate constant, $k$ ( $\text{sec}^{-1}$ )
Incubation	$5.2 \times 10^{-5}$
Ultraturrax	$9.1 \times 10^{-5}$

For Sucrose:

$$k_{\text{ultraturrax}}/k_{\text{incubator}} = 1.75$$

# Molassa (Sucrose+glucose+fructose) fermentation



Method	Reaction rate constant, $k$ ( $\text{sec}^{-1}$ )
Incubation	$2.6 \times 10^{-5}$
Ultraturrax	$5.5 \times 10^{-5}$

For Molassa:

$$k_{\text{ultraturrax}}/k_{\text{incubator}} = 2.07$$

**Molassa is a better feedstock for ethanol production**

## Effect of additive and pH on fermentation rate

Reaction: Glucose fermentation

Method: Ultraturrax

Additive: Activated carbon

pH: 2 and 6

Fermentation condition	Reaction rate constant, $k$ ( $\text{sec}^{-1}$ )
With activated carbon	$0.48 \times 10^{-5}$
Without activated carbon	$0.61 \times 10^{-5}$
At pH 2	$0.48 \times 10^{-5}$
At pH 6	$0.50 \times 10^{-5}$

**Addition of activated carbon has no effect on rate.**

**Reaction rate is almost same at pH 2 and 6.**

## Effect of yeast shelf life on fermentation rate

Yeast	Stirring speed, rpm	Reaction rate constant, k (sec <sup>-1</sup> )	$k_{\text{fresh}}/k_{\text{old}}$
Old	5,000	$0.61 \times 10^{-5}$	3.28
Fresh	5,000	$2 \times 10^{-5}$	
Old	10,000	$0.68 \times 10^{-5}$	5.88
Fresh	10,000	$4 \times 10^{-5}$	

**Shelf life of yeast significantly affects the fermentation rate. Fresh yeast's performance is 6-fold higher than old yeast with nearly 6 months of shelf life.**

---

## **Main results with Ultraturrax**

- A new method for acceleration of fermentation rate is developed
  - Enhancement in fermentation rate was observed for glucose (monosaccharide), sucrose (disaccharide), and molassa (a mixture of glucose, fructose, and sucrose) by using ultraturrax
  - Molassa is a preferred feedstock with higher acceleration in fermentation rate by using ultraturrax
  - Yeast with long shelf life reduced the fermentation rate
  - Addition of activated carbon or alteration of pH from 2 to 6 showed no acceleration in fermentation rate
  - Future studies involve fermentation of hydrolyzates from biomass using ultraturrax
-

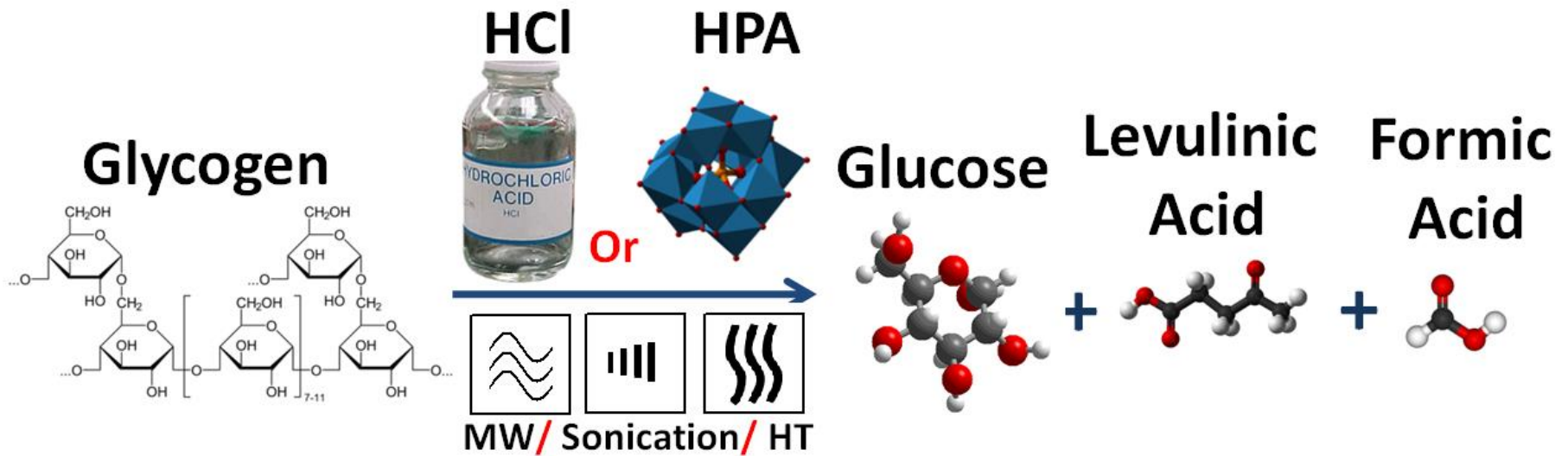
---

# Can Glycogen be a Renewable Feedstock for Glucose?

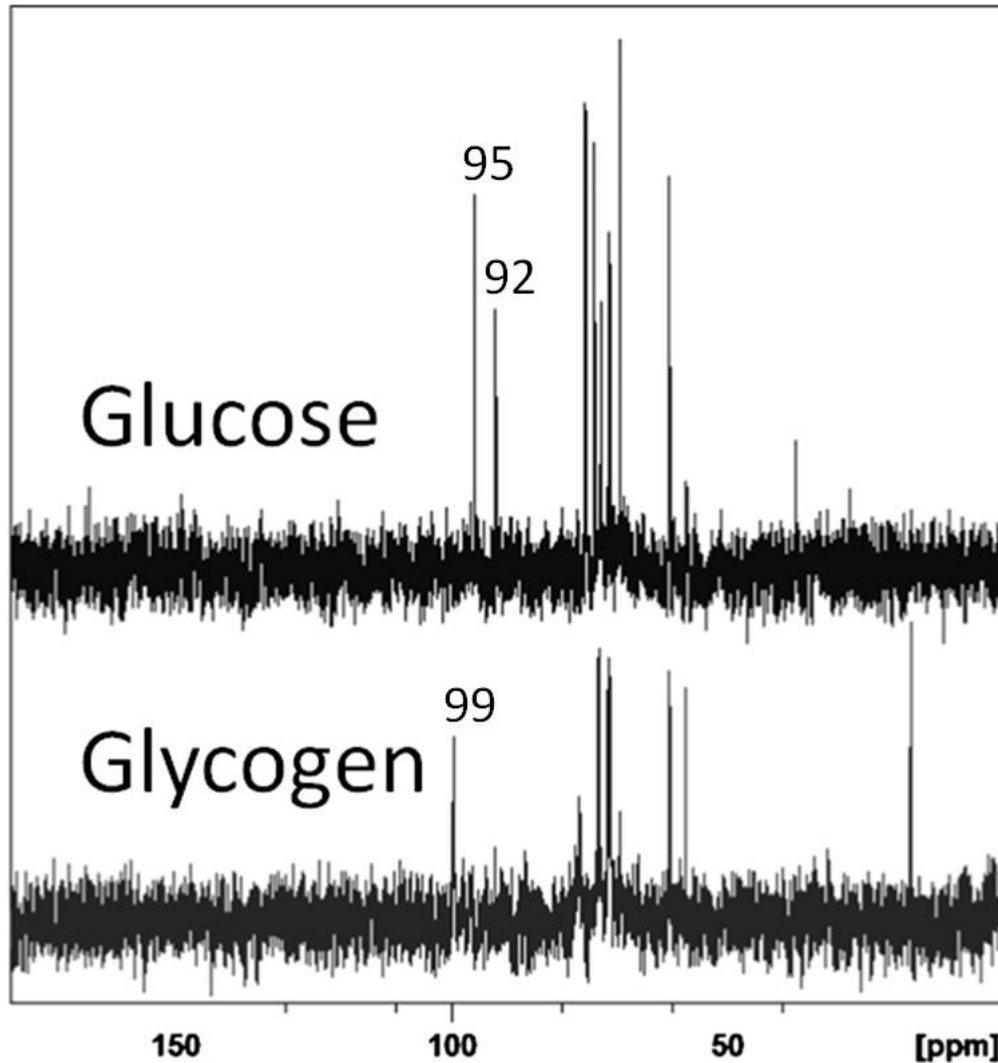
## Hypotheses & Research goals

- If glycogen could be a sustainable feedstock for glucose production.
- If microwave and sonic irradiation accelerate glycogen hydrolysis to glucose.
- If heteropoly acids (HPA's) catalyze glycogen hydrolysis.

# Glycogen conversion process



# Glycogen hydrolysis with microwave



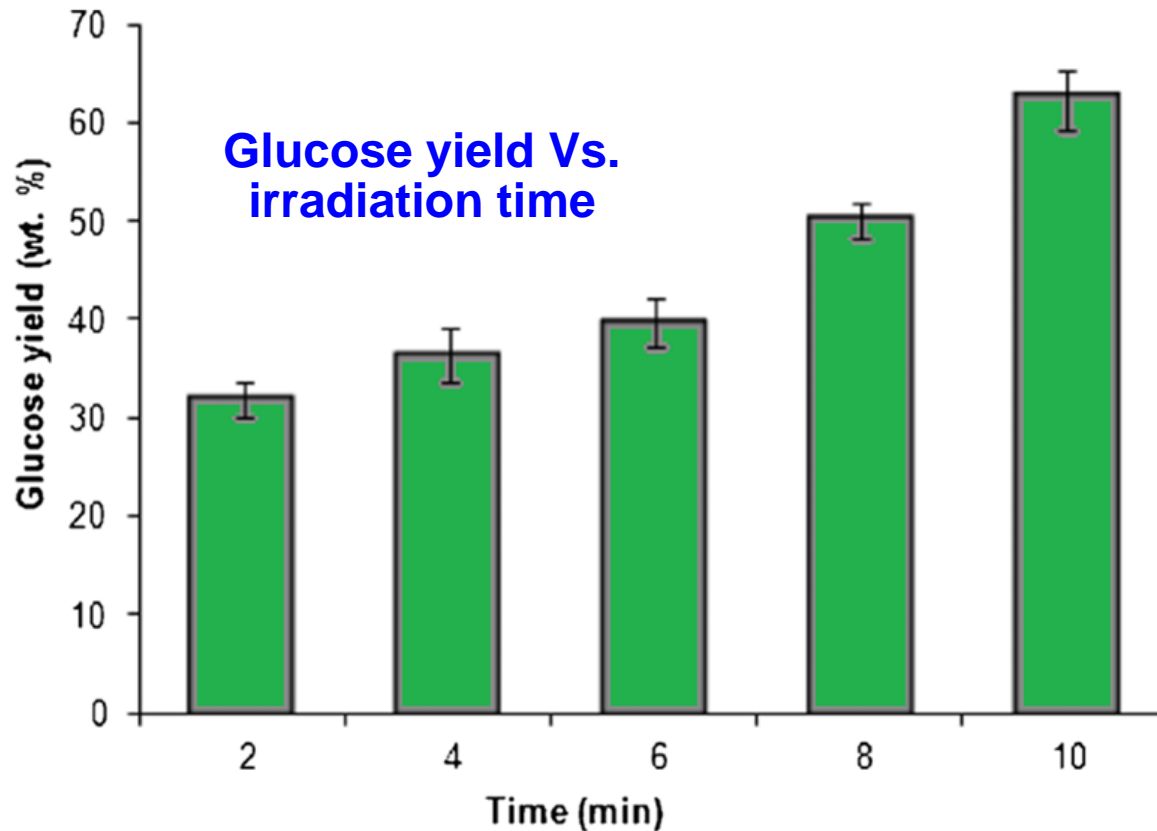
## Hydrolysis conditions

- Catalyst: HCl
- Irradiation time: 10 min.
- Reactant/catalyst:  
0.2 g glycogen in 10 mL 1 M HCl.
- Hydrolyzate  $^{13}\text{C}$  NMR analysis: Glycogen converted to glucose

**In 10 min. glycogen converts to glucose**



# Glucose yield – HPLC analysis



## Hydrolysis conditions

Glycogen amount: 0.4 g in 20 mL 1M HCl.

Irradiation time: 2 - 10 min.

Glucose yield increased from 32 to 62 wt.% as the reaction time increased from 2 to 10 min.

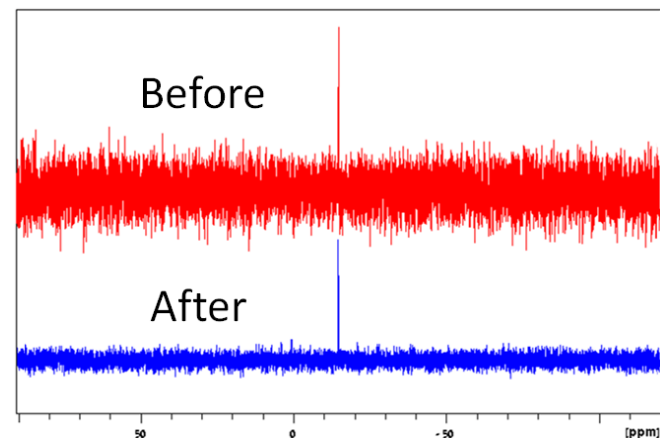
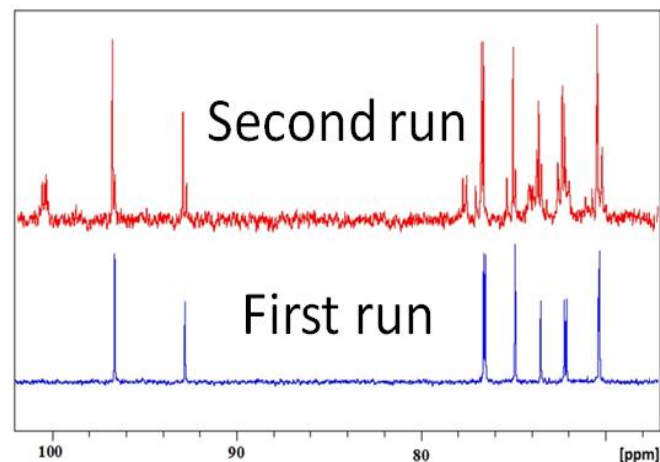
# Can HPA's replace HCl?

## Hydrothermal reaction

- 1 g glycogen with 1 g HPW in 40 mL water at 120 °C for 4 h
- Complete conversion of glycogen to exclusively glucose
- Catalyst regeneration by extraction of HPW with diethyl ether

## Reusability of catalyst

- 0.25 g glycogen with 0.25 g HPW in 10 mL water
- Catalyst stable after use ( $^{31}\text{P}$  NMR)
- Microwave irradiation accelerated the hydrolysis (10 min Vs. 2h in hydrothermal and more than 6h in sonication)



$^{31}\text{P}$  NMR spectra (Typical peak of P at -12 ppm Keggin type poly anion)

**HPA's are green and reusable catalysts for the production of glucose from polysaccharides**

---

## Conclusions

- Glycogen was converted to glucose in 10 min.
- Use of microwave accelerated hydrolysis.
- Hydrothermal method is selective towards glucose.
- HPA's are green and reusable catalysts for glycogen hydrolysis.

## Further studies

- Production of glycogen from CO<sub>2</sub>.
- Use of catalysts like ionic liquids, zeolites, amylase

# Biomass as feedstock for ethanol



*Pinus radiata*



Cotton



*Cicer arietinum*



Sugar cane bagasse

*Biomass*

*ethanol*

# Delignification of Biomass



*Pinus radiata*, 10 g

0.125 M NaOH, 100  
mL, 70 °C, 1 h

→  
delignification

Halocellulose  
7.2 g



*Cicer Arietinum*, 10 g

0.125 M NaOH, 100  
mL, 70 °C, 1 h

→  
delignification

Halocellulose  
6.27 g

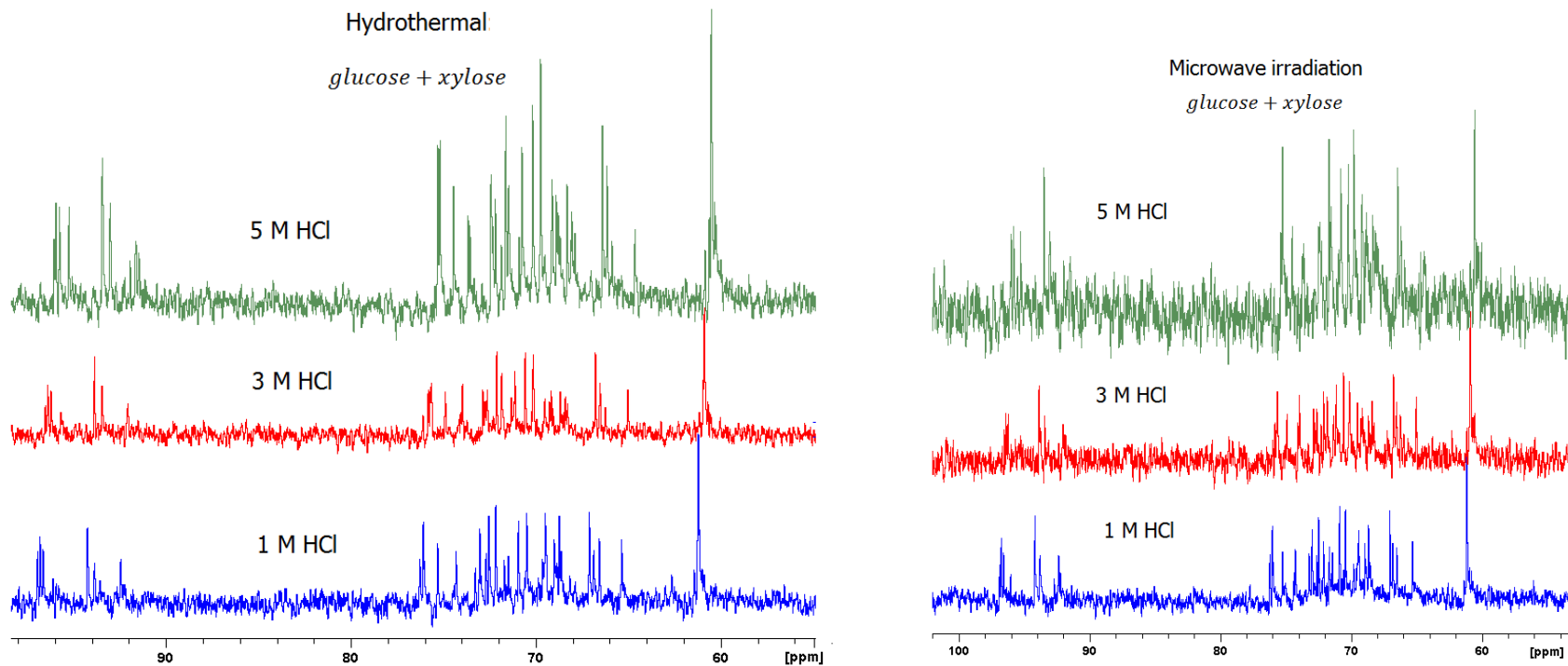
# Ethanol from *Pinus radiata*

## Hydrolysis of Halocellulose

Reactant: 0.5 g

Hydrothermal: 120 °C, 1 h, 10 mL HCl

Microwave irradiation: 10 mL HCl, 5 min.,



**Microwave and hydrothermal methods yielded glucose and xylose**

# Hydrolysis of cellulose microwave Vs. hydrothermal

Method	Conc. HCl (M)	% conv. Of Halocellulose
Microwave	1	38
	3	42
	5	44
Hydrothermal	1	32
	3	40
	5	42



Faster hydrolysis with Microwave irradiation (5 min. Vs 1 h with hydrothermal)

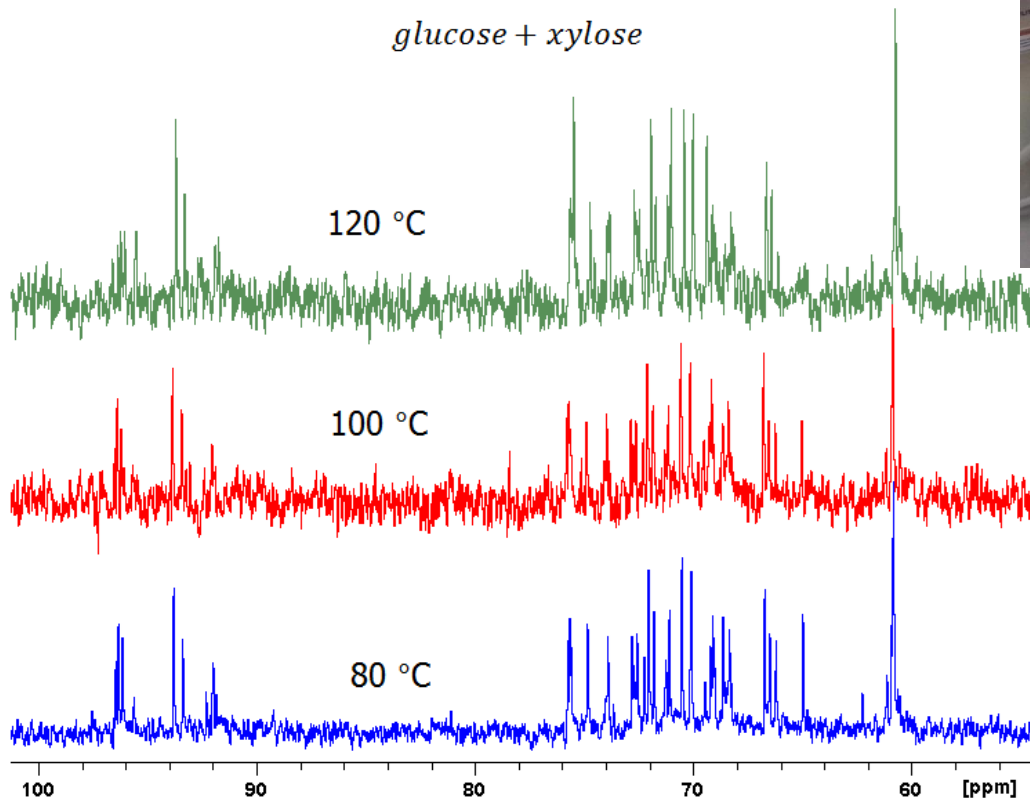
3 M HCl is the optimum concentration of acid

~ 40 wt.% halocellulose could be converted to glucose and xylose

# Hydrolysis of Halocellulose in commercial microwave

Reactant: 0.25 g  
Conc. HCl: 3 M, 10 mL  
Time: 10 min.

*glucose + xylose*



Temperature [°C]	Wt. % conv.
80	32
100	36
120	46

46 wt.% conv. of halocellulose is observed in 10 min. irradiation on commercial microwave oven



# Fermentation of hydrolyzate from *Pinus radiata*

Hydrolysis conditions

Reactant: 3 g

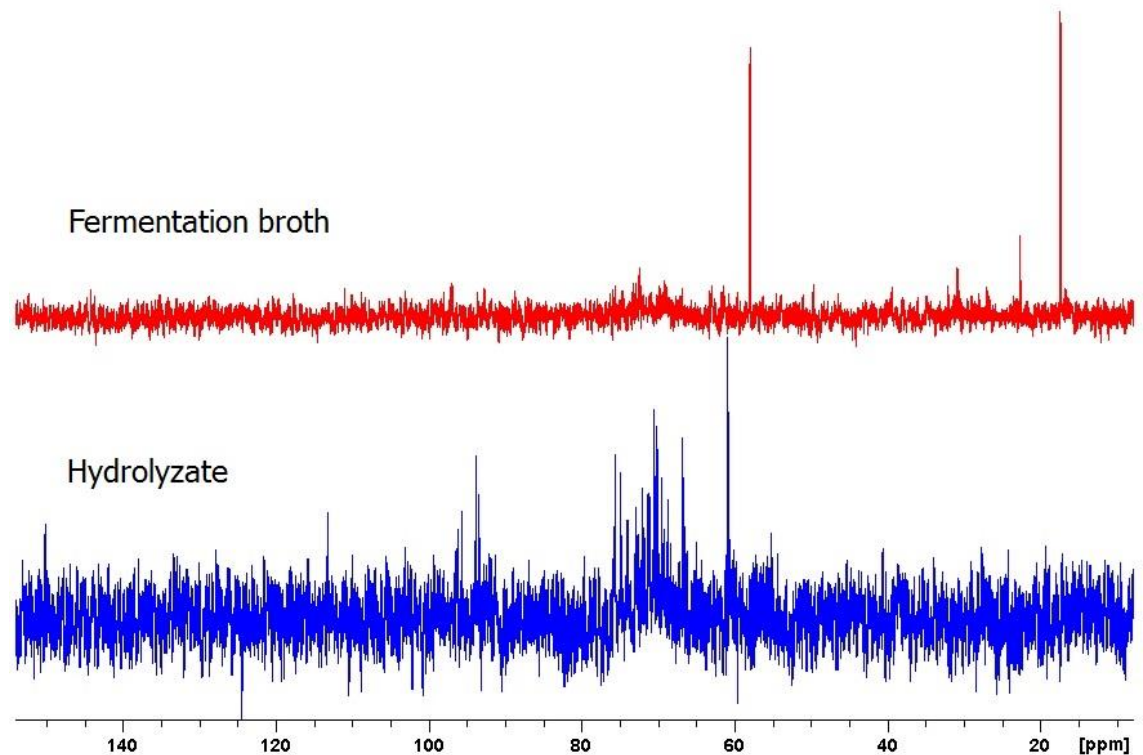
Irradiation: 15 min

HCl: 3 M, 60 mL

Fermentation

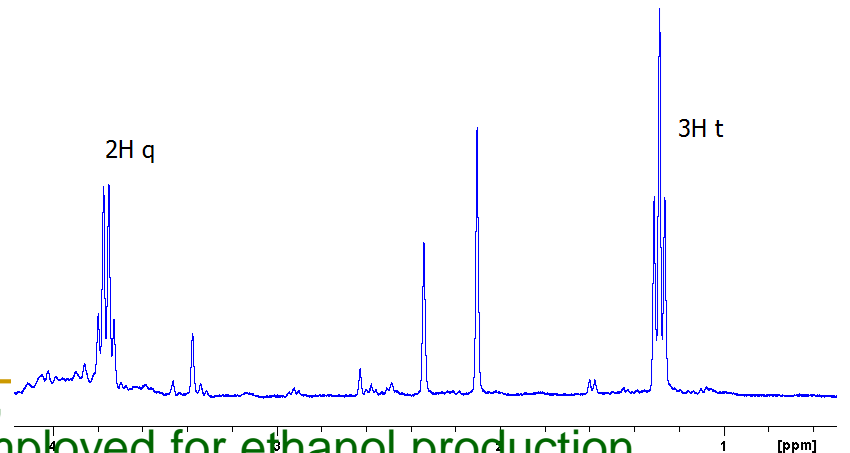
Neutralization of hydrolyzate

2 g yeast



**Glucose and xylose completely converted to ethanol**

In addition to *Pinus radiata*, *Cicer arietinum*,  
Sugar cane bagasse and cotton are also employed for ethanol production



---

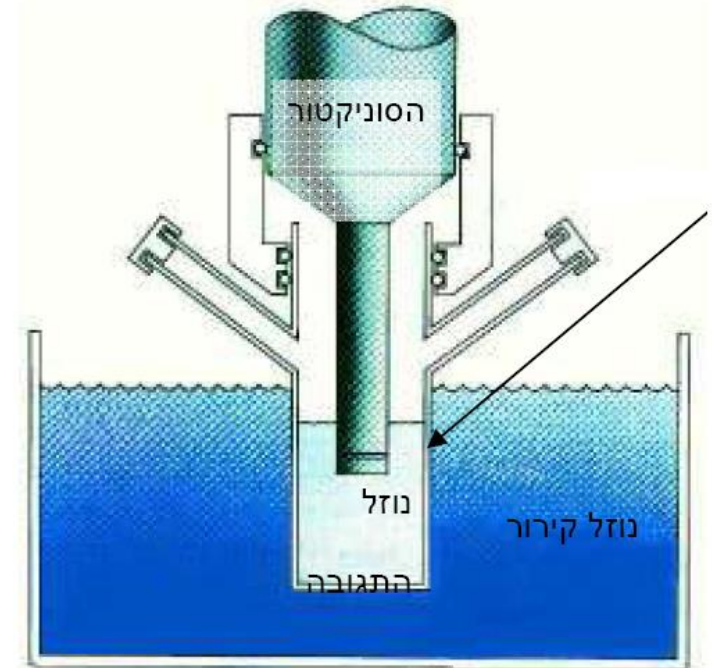
## Bioethanol from Biomass

In addition to the terrestrial lignocellulosic biomass, like *pinus radiata*, *cicer arietinum*, sugar cane bagasse, a variety of marine alga like *chlorilla*, *ulva lactuca* and *saragassum* were converted to bioethanol.

The marine alga, *saragassum* stands out with an ethanol yield as high as 18 wt.%

---

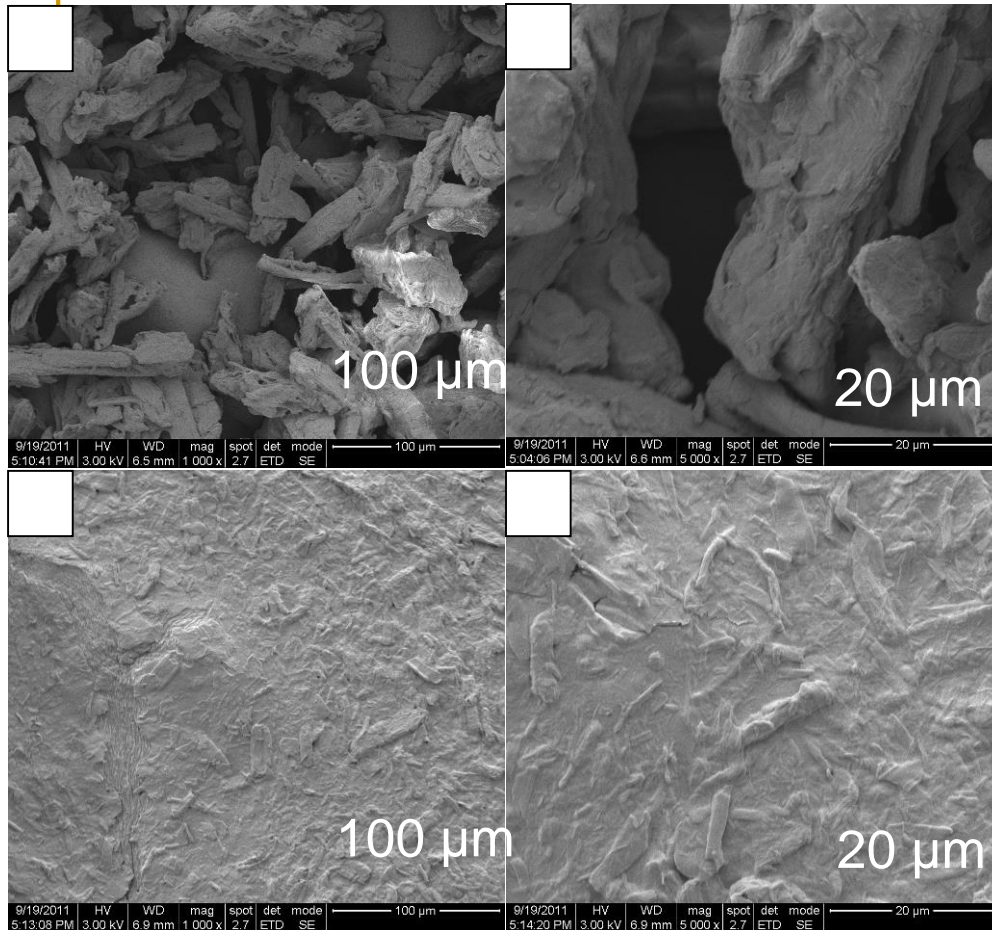
## Decomposition of cellulose under microwave irradiation



תרשים כללי של מערכת הסונוכימית

Pictorial representation of the 10 wt.% cellulose powder in water  
(a) before and (b) after sonication

# SEM analysis of cellulose before and after sonication



**Before sonication**

**After sonication**

## SEM images of the 10 wt.% cellulose (Avicel) powder in water

**Sonication had a profound influence on the morphology of the cellulose material** ➤  
**Cellulose particles which appeared like blocks and logs of wood changed to thin** ➤  
**layers upon sonication for 1h**  
**Change in the physical form of the  $\alpha$ -cellulose was attributed to the** ➤  
**disruption of the hydrogen bonding network**

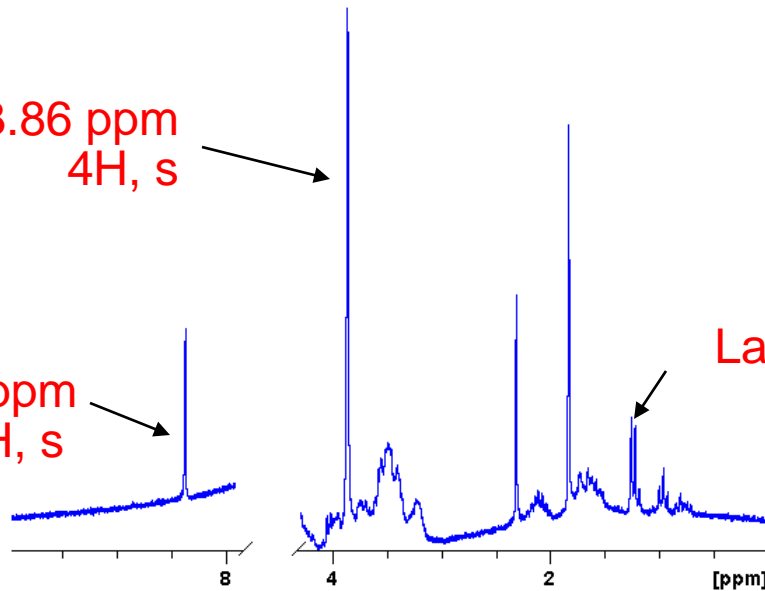
# Microwave irradiation of 1 wt. % cellulose in the presence of NaOH

Ethylene glycol, 3.86 ppm  
4H, s

**<sup>1</sup>H NMR**

Formic acid, 8.3 ppm  
1H, s

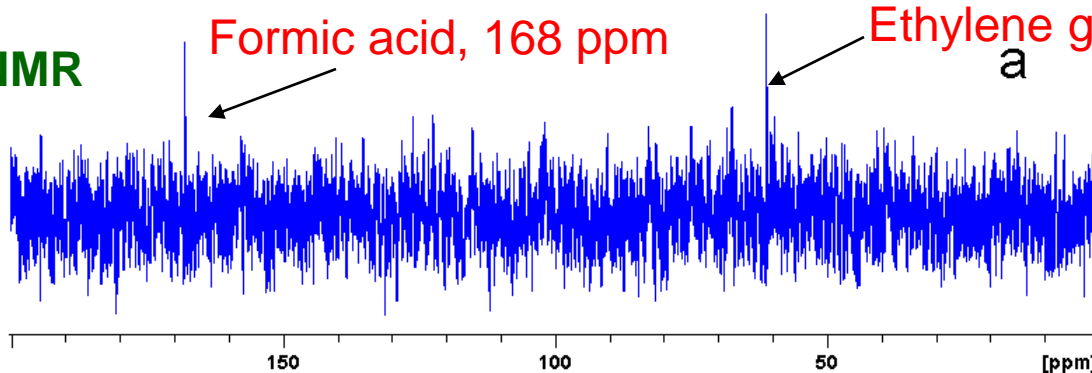
Lactic acid, 1H, d (1.18, 1.2 ppm)



**<sup>13</sup>C NMR**

Formic acid, 168 ppm

Ethylene glycol, 61.1



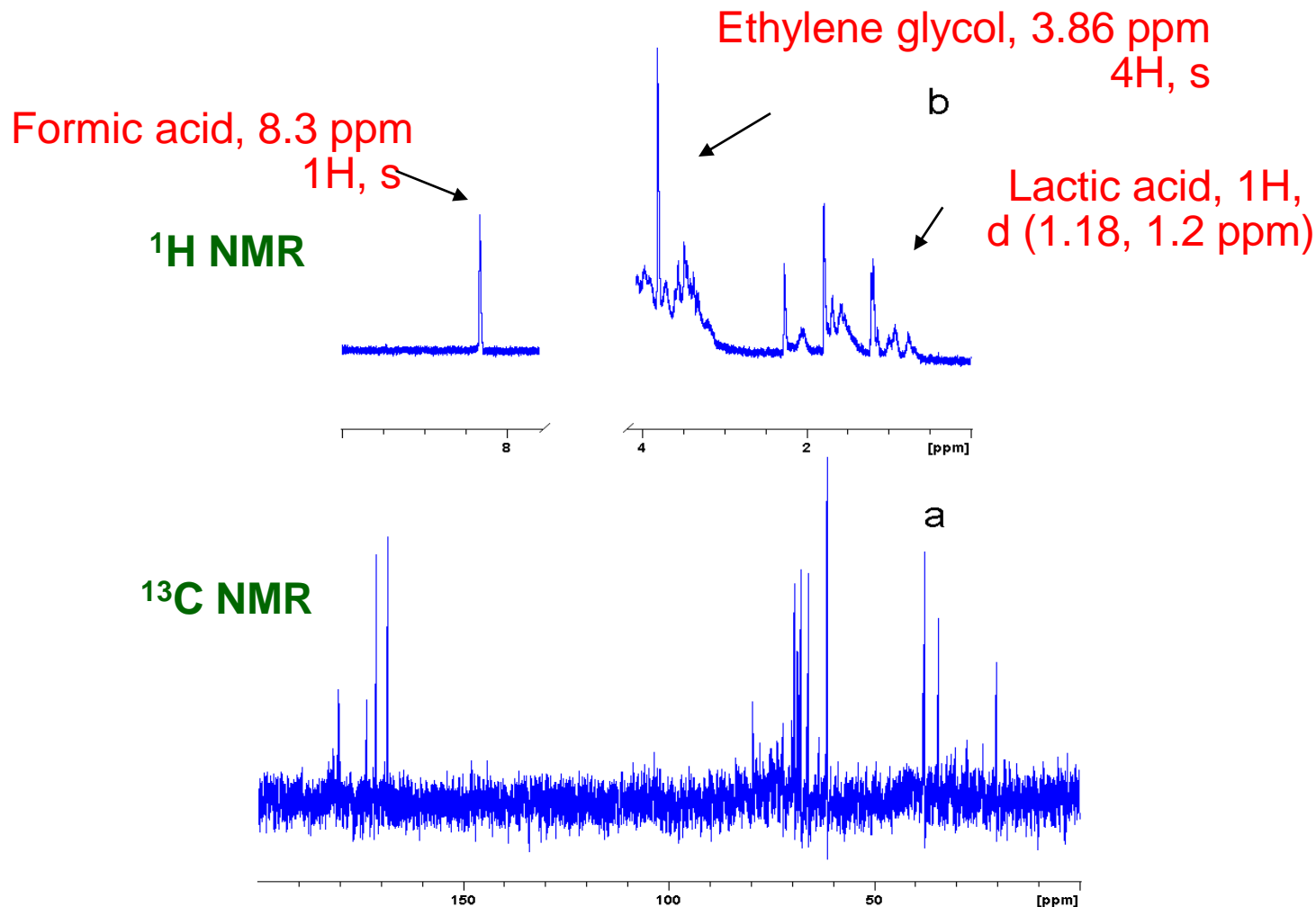
**NMR spectra of reaction product from cellulose (1 wt.%) degradation**

**10 mL, 1 (wt.%) cellulose dispersion with 0.1 g NaOH exposed to microwave irradiation for 5 minutes**

**44 wt.% conversion of cellulose observed**

**Ethylene glycol, formate, lactate and acetate were observed as cellulose decomposition products**

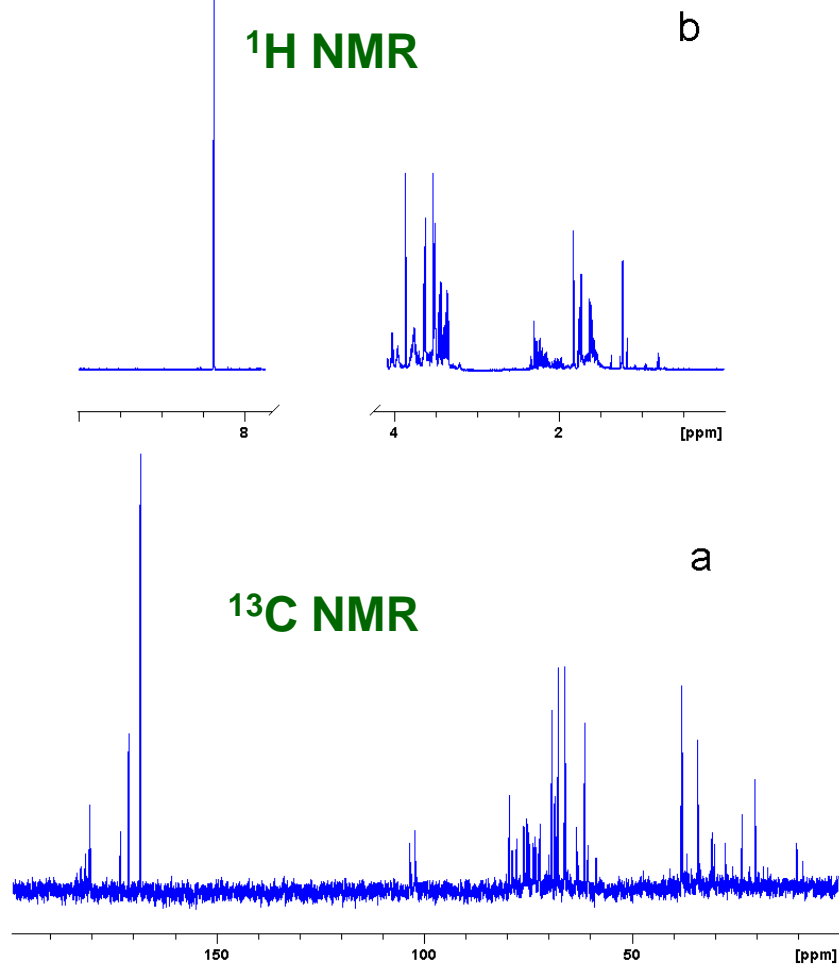
# Microwave irradiation of 4 wt. % cellulose



## NMR spectra of the reaction product from 4 wt.% cellulose

*Product distribution obtained is similar to that of 1 wt.% cellulose dispersion* ➤  
*58 wt.% conversion of cellulose is observed upon irradiation for 5 minutes* ➤  
*In addition to ethylene glycol, formic acid and lactic acid, isosaccharinic acid is also* ➤  
*observed*

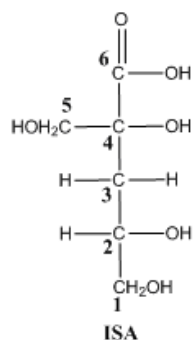
# Microwave irradiation of 10 wt. % cellulose



## NMR spectra of the reaction product from 10 wt.% cellulose

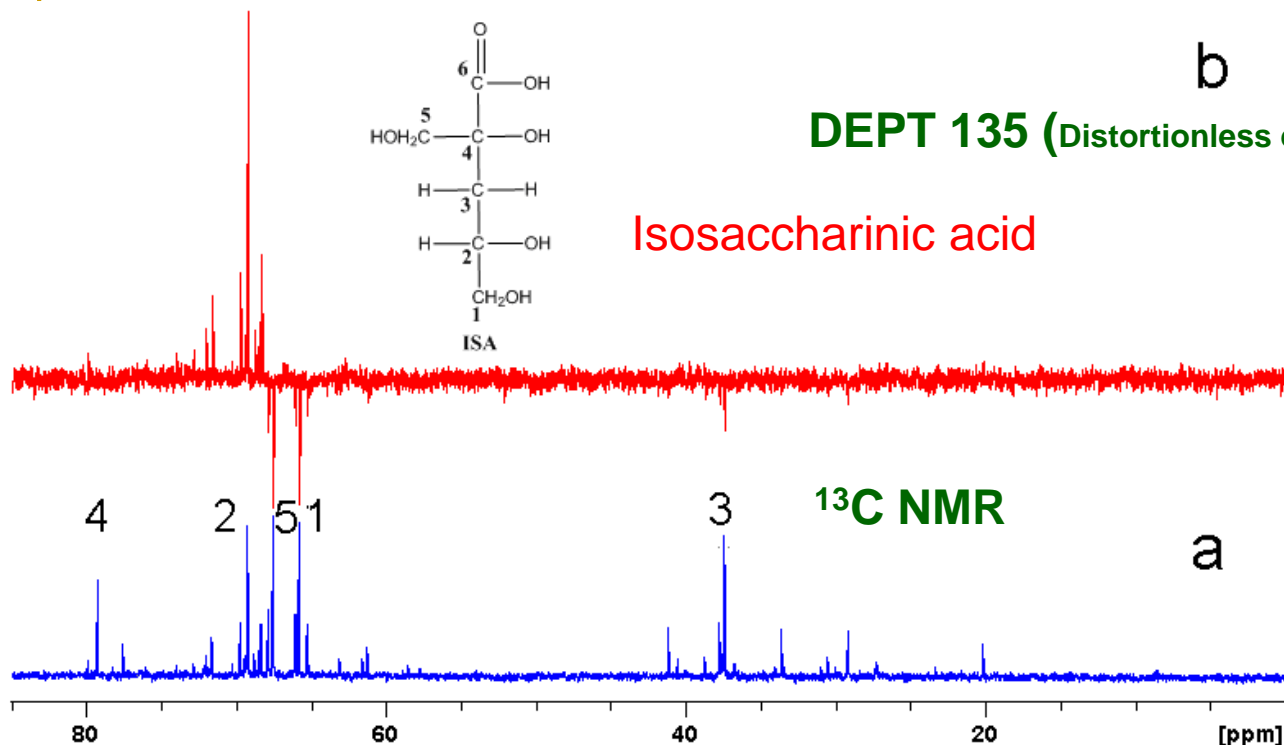
*Product distribution obtained is similar to that of 1 wt.% cellulose dispersion* ➤  
*54 wt.% conversion of cellulose is observed upon irradiation for 5 minutes* ➤  
*In addition to ethylene glycol, formic acid and lactic acid, isosaccharinic acid is also* ➤  
*observed*

# Isosaccharinic acid – the reaction intermediate of Cellulose degradation



**DEPT 135** (Distortionless enhancement by polarization transfer)

Isosaccharinic acid



**NMR spectra of the reaction product from 10 wt.% cellulose upon microwave irradiation for 30 seconds**

*DEPT studies reveal the substitution of carbon atoms in a compound ➤  
In DEPT 135, CH and CH<sub>3</sub> appear as positive peaks and CH<sub>2</sub> will appear as negative ➤  
10 wt.% cellulose dispersion exposed to microwave for 30 sec to know the ➤  
reaction intermediate  
The reaction product exhibited peaks typical of Isosaccharinic acid ➤  
(37.5, 65.7, 67.5, 69.2 and 79.2 ppm)  
Thus isosaccharinic acid is the reaction intermediate in the degradation of cellulose ➤*



---

## Summary:

1. The study comprises of employing highly crystalline commercial cellulose (Avicel®) for the production of chemicals like formic acid, ethylene glycol and lactic acid.
  2. The strategy for decomposing cellulose comprises of two stages: (i) to reduce the crystallinity of cellulose by sonication and (ii) expose the aqueous dispersions of cellulose in alkaline medium to microwave irradiation for a maximum of 5 minutes.
  3. The developed method is applicable for 1, 4 and 10 wt.% cellulose (initial concentration) aqueous dispersions. The wt. % conversion values of 44, 58 and 54 % were observed with 1, 4 and 10 wt.% cellulose dispersions.
  4. Thus an easy and fast process has been developed for the degradation of cellulose to small organic molecules with the aid of sonication and microwave irradiation under alkaline (NaOH) conditions.
-

## Chemical reduction of CO<sub>2</sub> to HCOONa

Chemical reduction of carbon dioxide (CO<sub>2</sub>) to fuels and chemicals is one of the dream reactions of chemists. ➤

CO<sub>2</sub> is a very stable molecule (Standard free energy of formation,  $\Delta G^\circ = -394.3$  kJ/mol) ➤

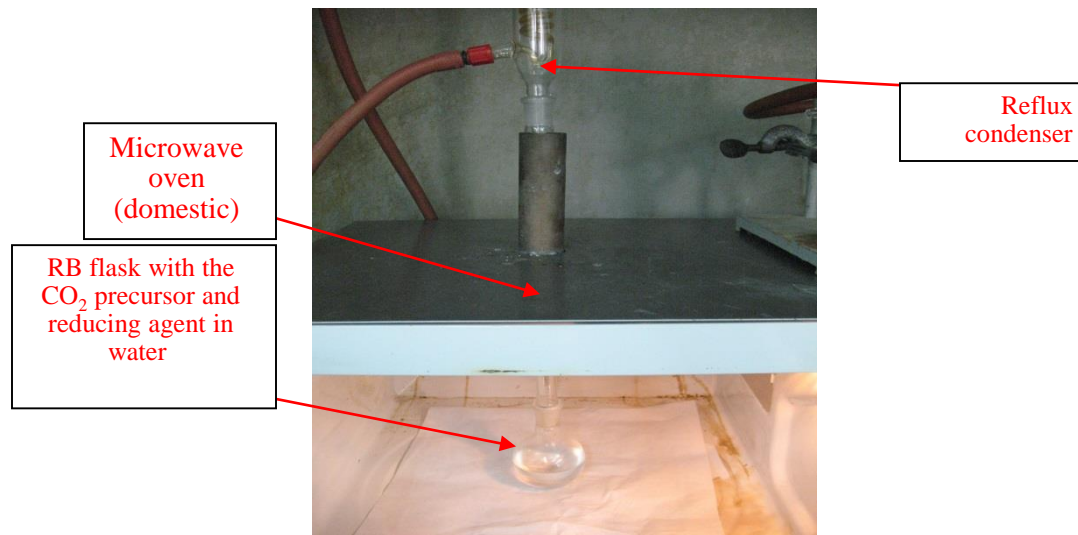
Transformation of CO<sub>2</sub> to chemicals not only reduces the major green house gas but also convert the same to a useful material. ➤

There are currently no known chemical reduction methods operating at modest reaction conditions to convert carbon dioxide to formate. ➤

Radiochemical, photochemical, electrochemical and bio photo electrochemical methods are known to yield formic acid from carbon dioxide. But none of the aforementioned approaches could be employed industrially. ➤

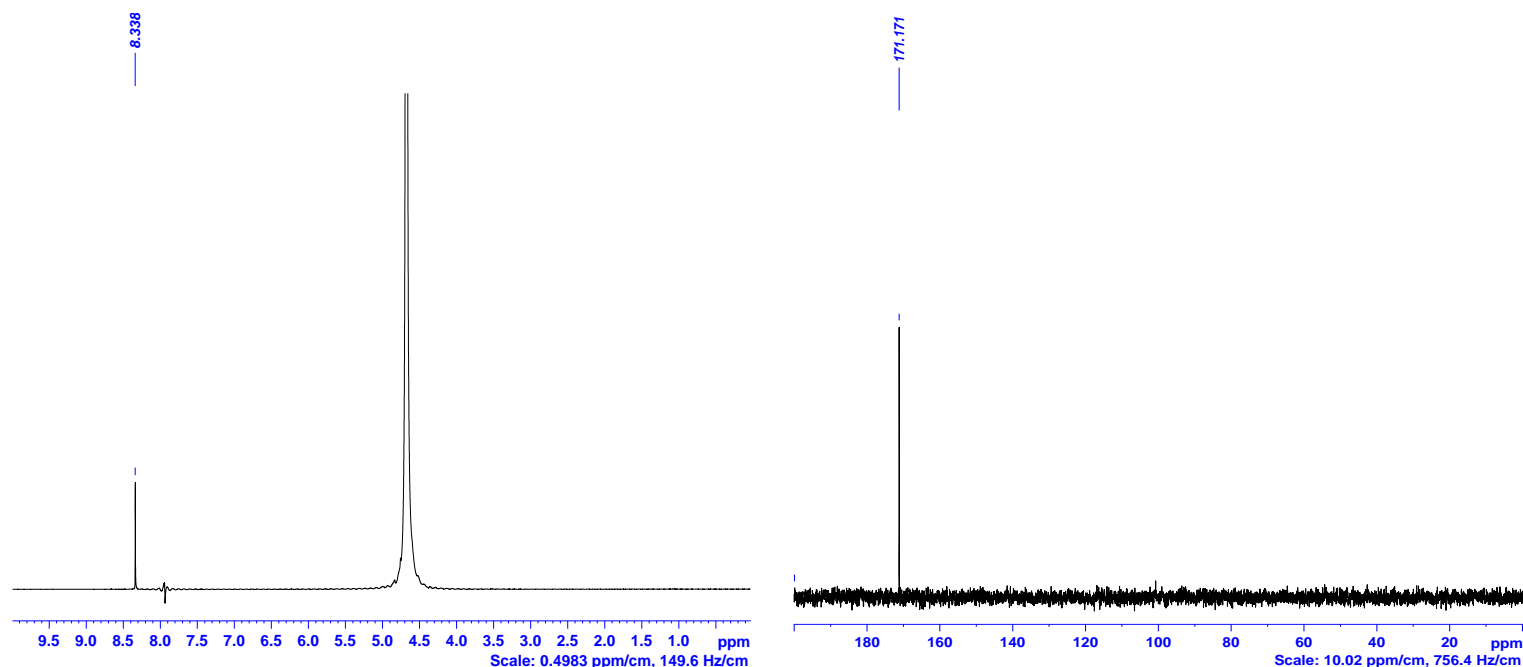
## Process for the chemical reduction of CO<sub>2</sub>

Typical process comprise of placing in a round bottom flask, 1.0 g ammonium carbonate (CO<sub>2</sub> precursor) and 0.5 g sodium boro hydride in 10 mL water and subsequently subjecting the contents to microwave irradiation for 5 minutes



Pictorial representation of the CO<sub>2</sub> conversion taking place under microwave irradiation

## HCOONa from CO<sub>2</sub> generated in situ from (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>



(a) <sup>1</sup>H NMR and (b) <sup>13</sup>C NMR spectra of reaction product from the chemical reduction of CO<sub>2</sub> (from ammonium carbonate)

A peak at 8.3 ppm in the <sup>1</sup>H NMR (Fig. 1a), 171 ppm in <sup>13</sup>C NMR (Fig. 1b) ➤ establish the presence of formate anion and rule out the presence of formaldehyde or methanol or even carbonic acid.

## Summary:

CO<sub>2</sub>, either generated in situ by the decomposition of ammonium carbonate or dry ice in aqueous medium is reduced selectively to formate using NaBH<sub>4</sub> as reducing agent under microwave irradiation for 5 minutes.

The exclusive formation of sodium formate as the CO<sub>2</sub> chemical reduction product is established authentically through <sup>1</sup>H, <sup>13</sup>C, DEPT-135 NMR, FT-IR and UV-Vis spectroscopic studies.

The chemical reduction process involving the conversion of CO<sub>2</sub> to formate in aqueous medium is fast owing to the use of microwave irradiation.

NaBH<sub>4</sub> is an efficient reducing agent for the reduction of CO<sub>2</sub> in aqueous medium under microwave irradiation conditions.

Thus a new technology is invented for the chemical reduction of the thermodynamically stable CO<sub>2</sub> molecule to be converted to a valuable fuel, formate, which can be used as such in fuel cells as a substitute of methanol or can be employed as a reservoir for hydrogen fuel or can be used as an industrial chemical.

---

## **Acknowledgements:**

I thank Prof. Ami Ben-Amotz from Seambiotic,

Dr. P. Indraneel,

Miri Koberg,

Miri Klein,

Barry Kimchi

The group of Prof. Dubinsky, Dr. Yaron Yehoshua, Dr. Yael Kinel

Dr. Alvaro Israel, NIO, Prof. Avigdor Abelson-TAU

Lior Korzen

Grants: The famous Prof. Zaban with the Internal grant, ISF,

Ministry of Science & Tech. (2 infrastructure grants one with

Prof. Dubinsky, and one with A. Israel), Ministry of Energy and

Water), Israel-Korea -MOS

---

