Greener Catalysts for Biodiesel Production

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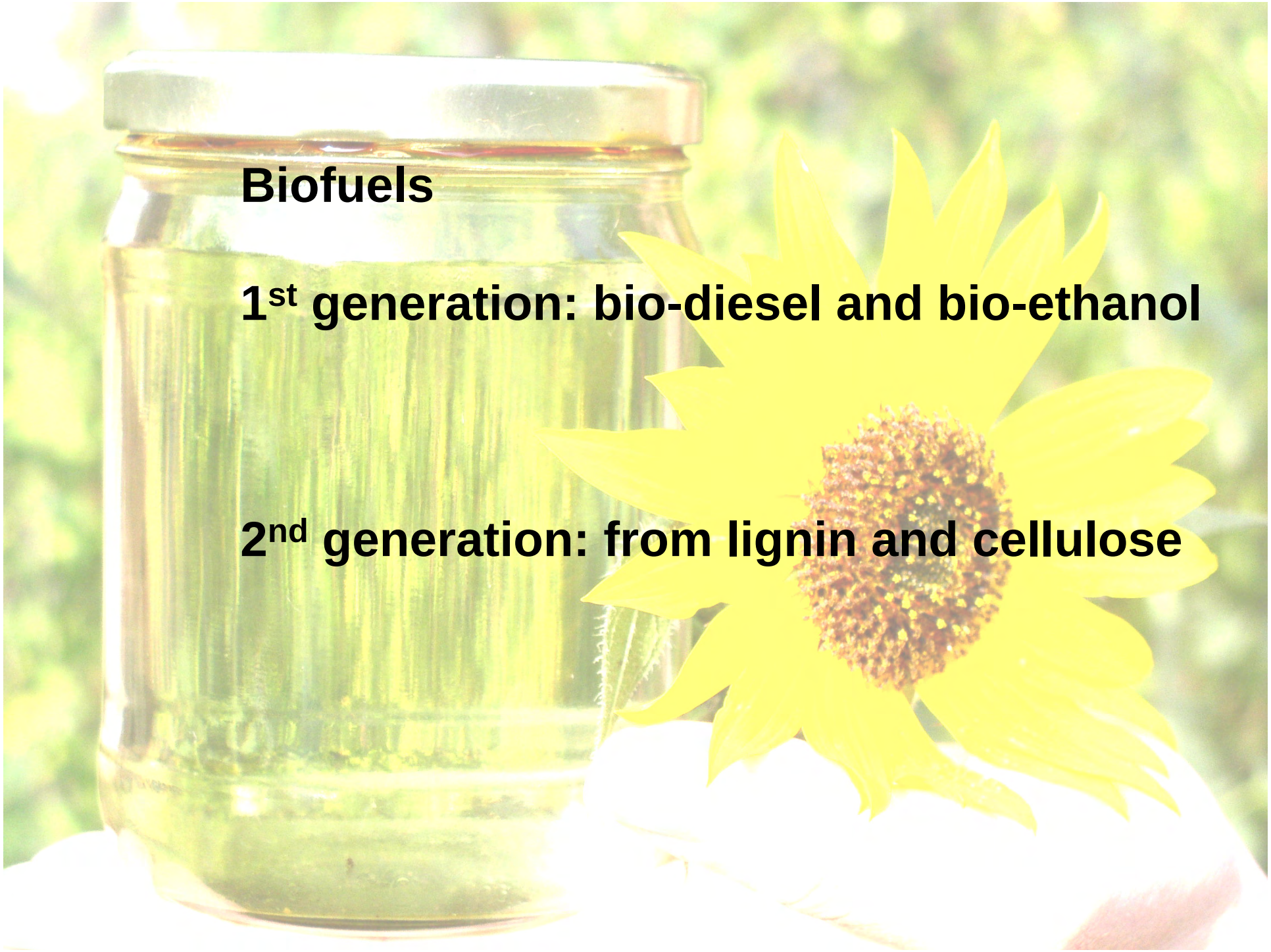


Biofuels

1st generation: bio-diesel and bio-ethanol

2nd generation: from lignin and cellulose

Renewable Transport Fuel Obligation (RTFO): 5 percent of all road vehicle fuel is from sustainable renewable sources by 2010

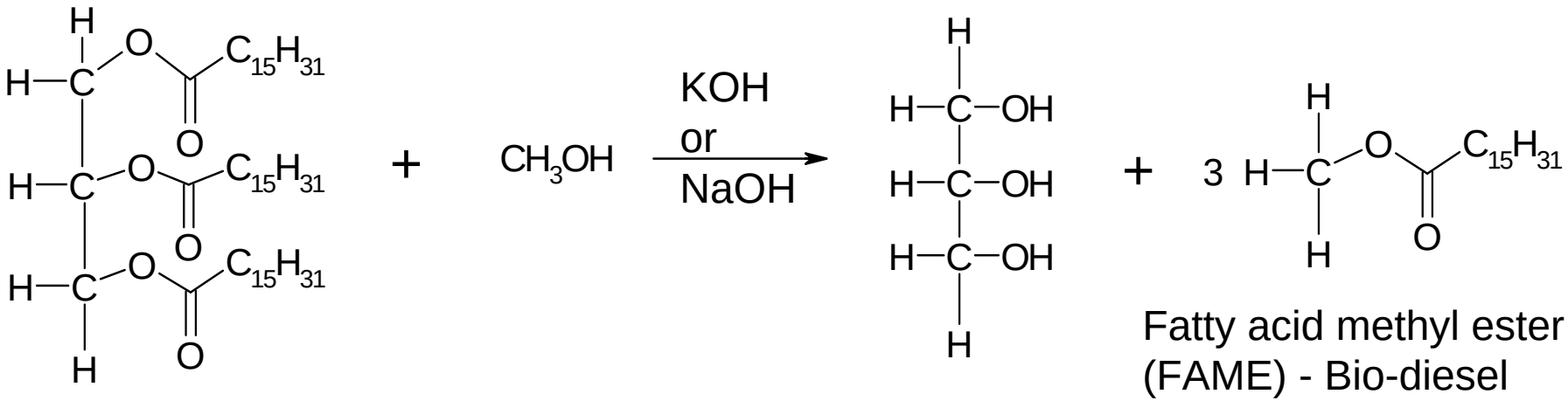
Biodiesel

Raw materials:	
Vegetable oils	70 p per litre
Recovered cooking oils	35 p per litre
H M Govt Duty	34 p per litre

Oil sources:	Rapeseed	950 litres per hectare
	Soybean (90% of US production)	700
	Sunflower	800
	Rapeseed	950
	Palm oil	4800
	Jatropha	2000
	Tallow	
	Algae	3000
	Chip shops, restaurants etc	

Conversion of vegetable oils to bio-diesel

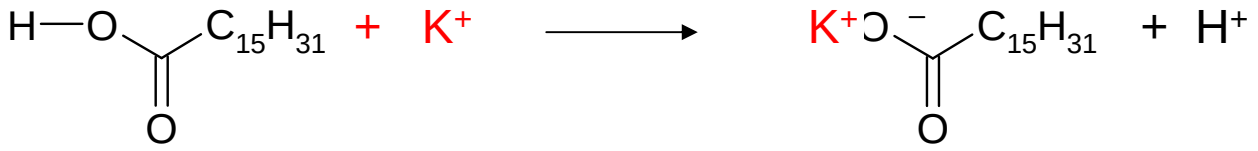
Major process: triglyceride to methyl esters



Triglyceride

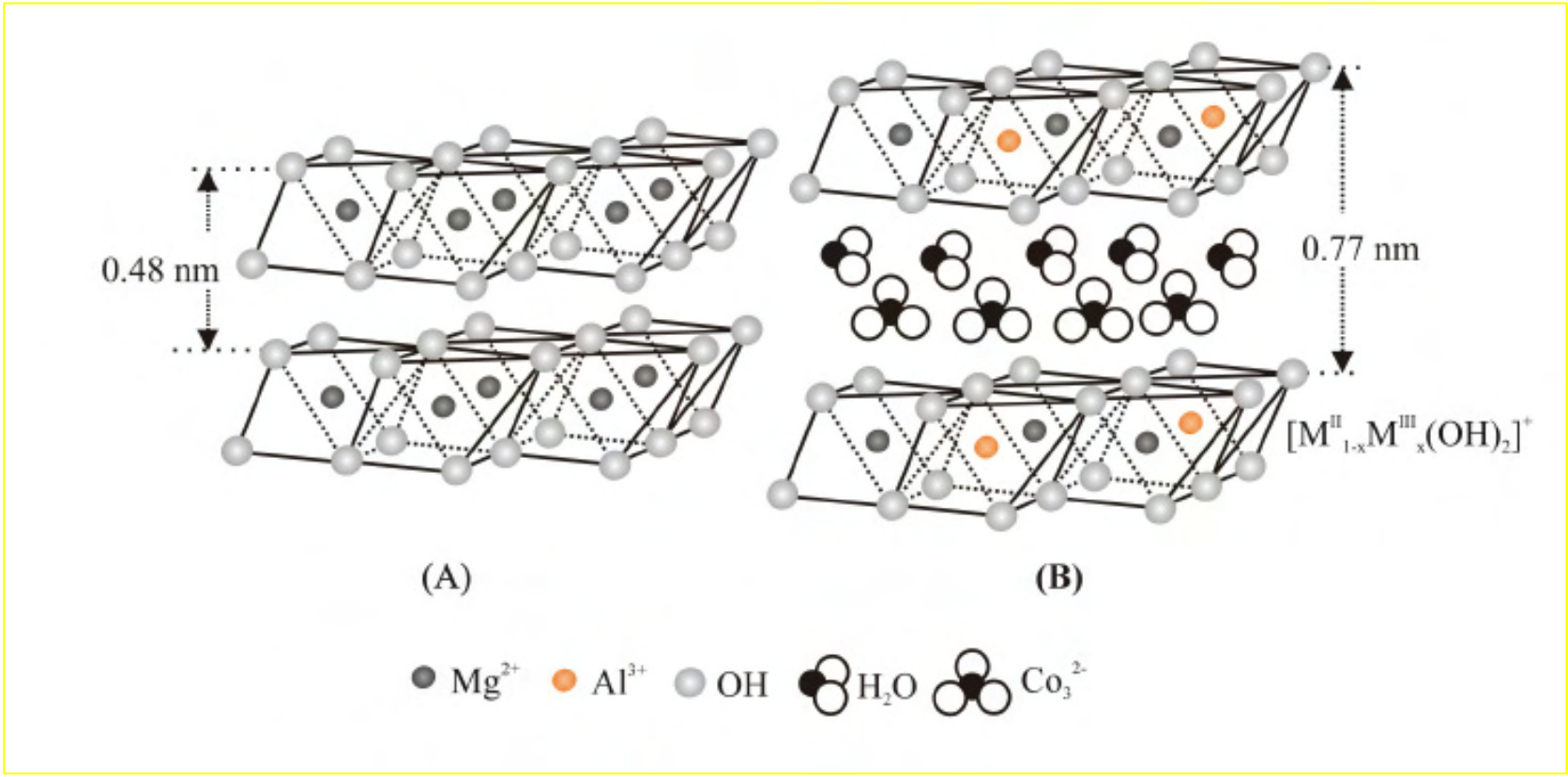
Fatty acid methyl ester (FAME) - Bio-diesel

Fatty acids, if present, they react with the KOH catalyst



Free fatty acid (FFA)

Fatty acid salt - soap

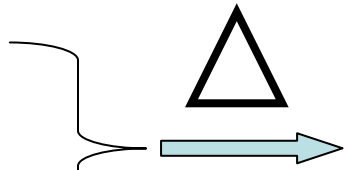


Layered double hydroxides (LDH's)

$[Mg(OH)_2]$ Brucite-like layers

Hydrotalcite: Mg_3Al

Many other examples: eg $Cu_{0.6}Mg_{2.4}Al$



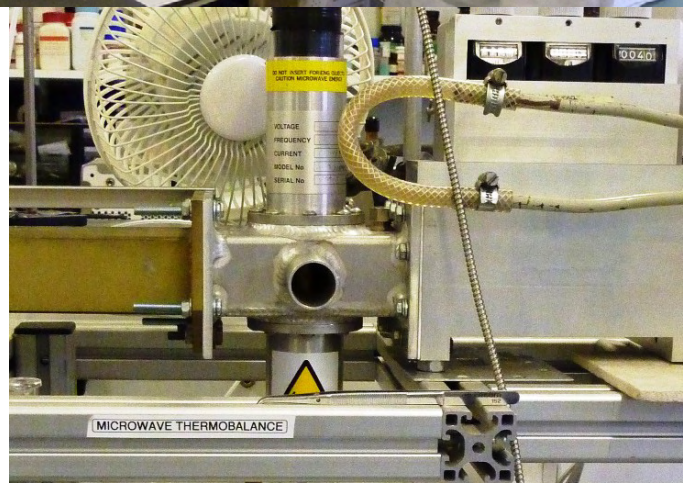
mixed metal oxides

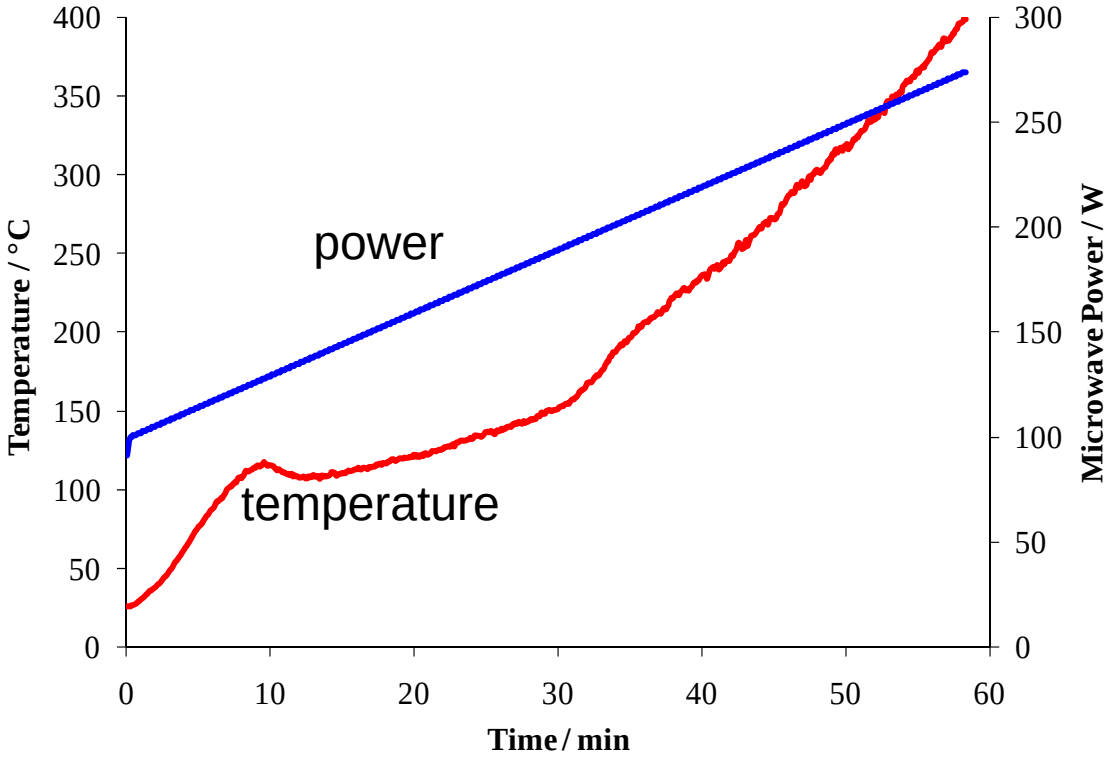
Calcining With Microwaves

$Cu_3Mg_3Al_2(CO_3)(OH)_{16}.4H_2O$

➔ $Cu_3Mg_3Al_2O_9 + 12H_2O + CO_2$

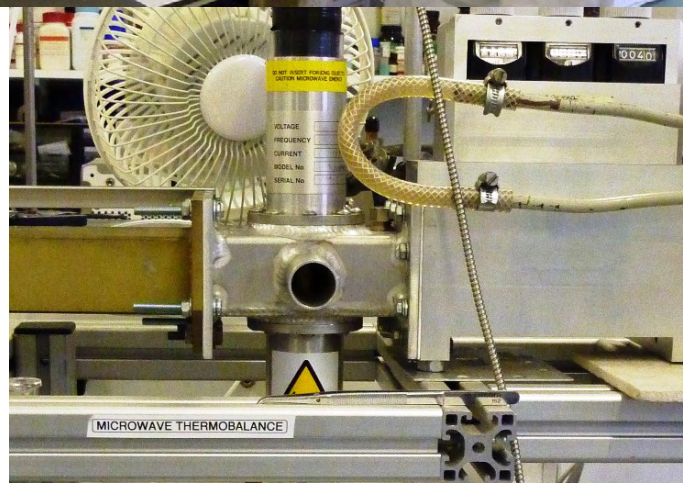
Microwave heating:
linear power increase

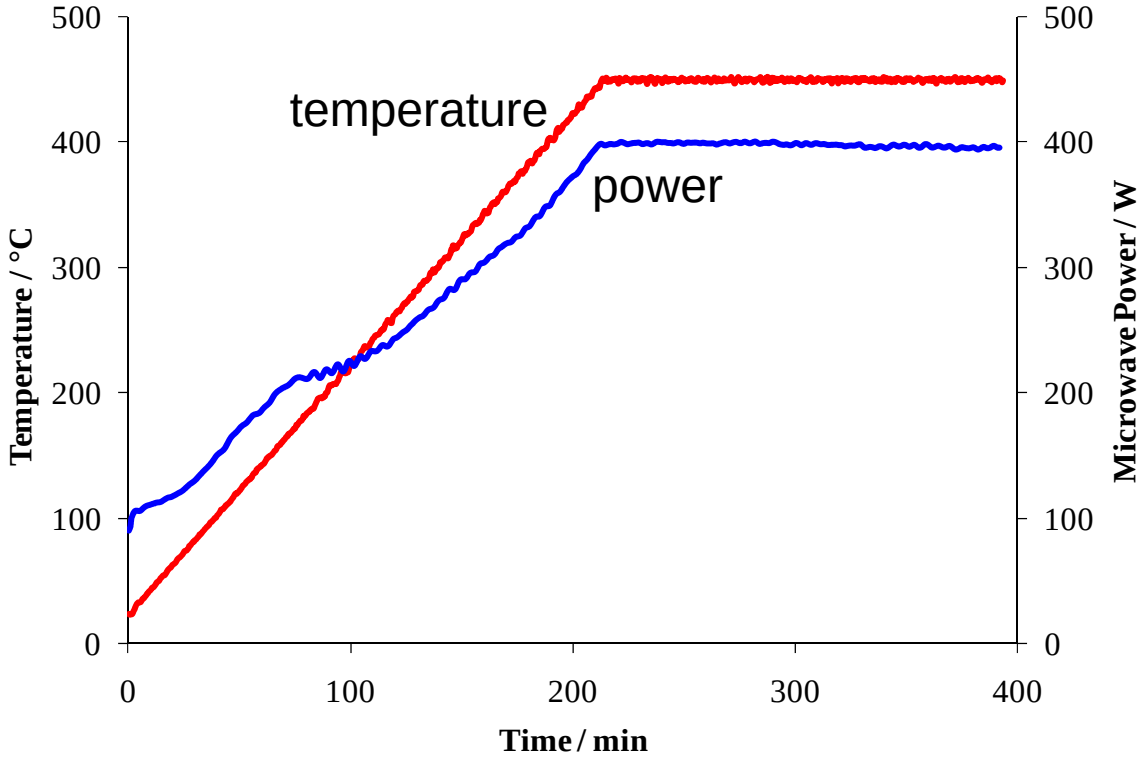




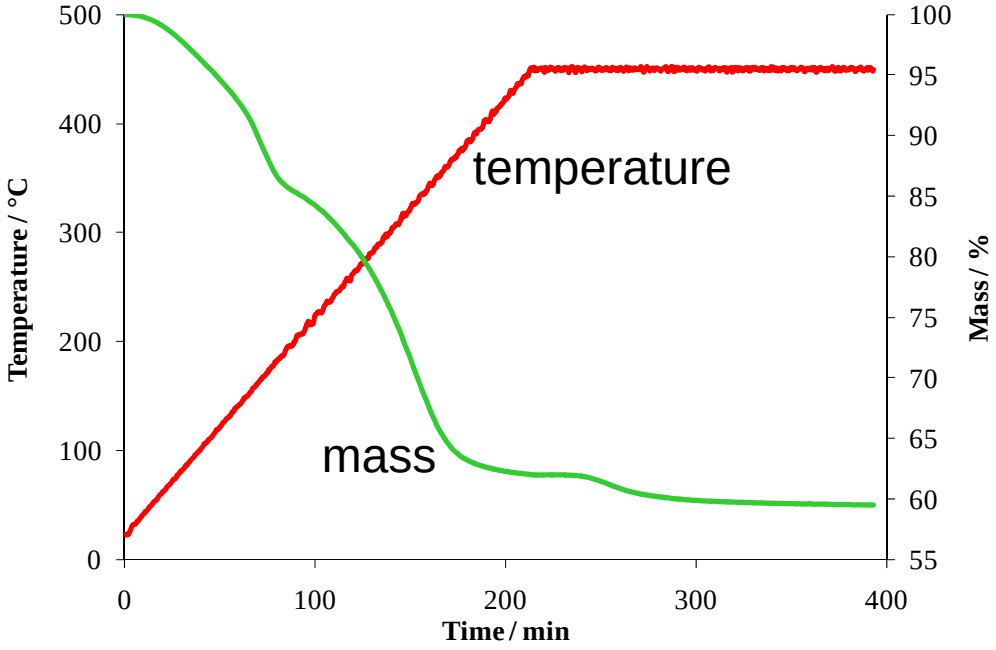
Calcining With Microwaves

Feedback control of microwave power to maintain constant rate of temperature increase

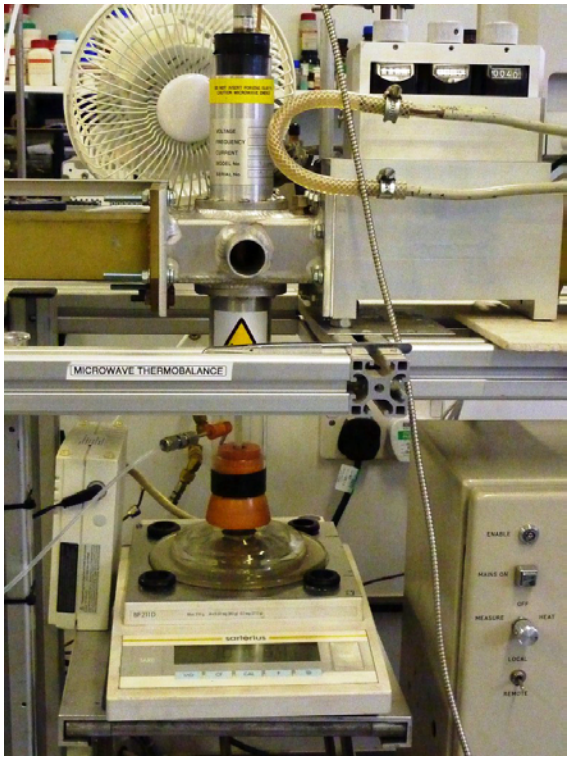


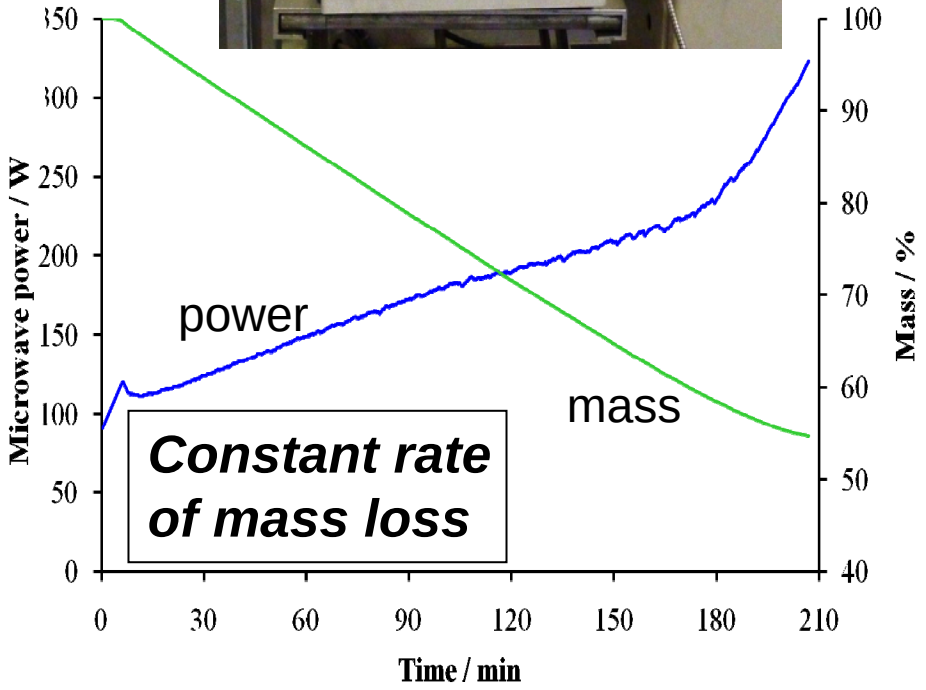


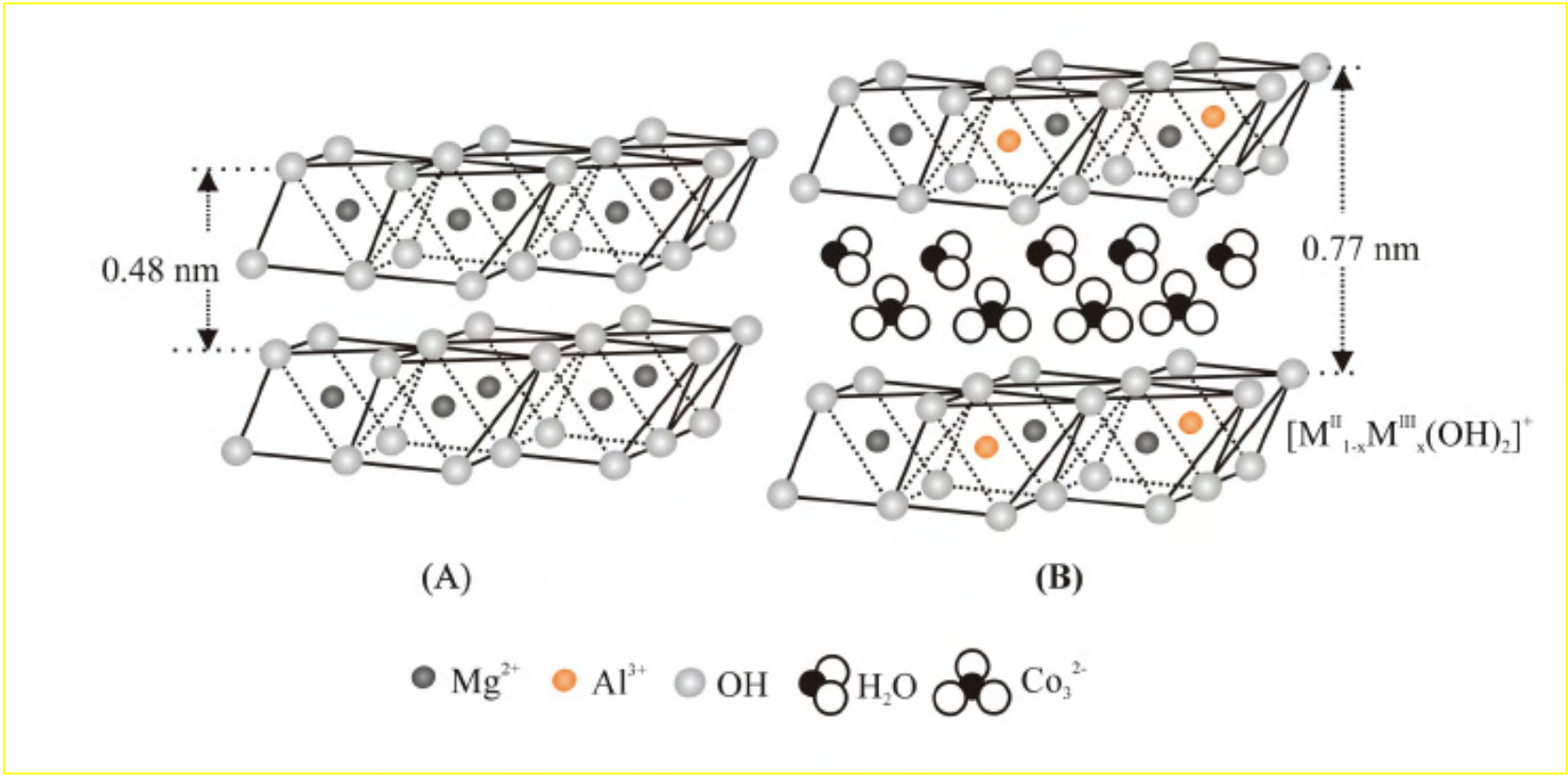
Calcining With Microwaves



Microwave power can be *feedback controlled* to maintain constant rate of *mass loss*







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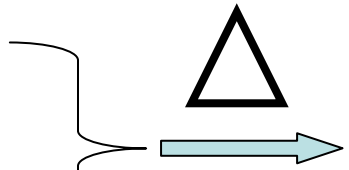
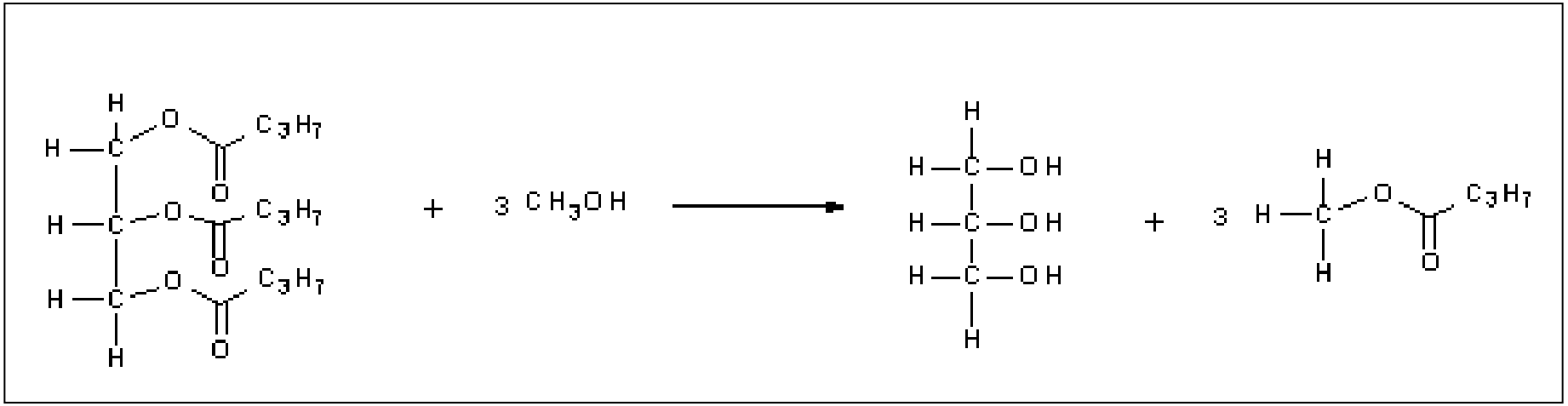


mixed metal oxides

Catalytic activity testing

Transesterification of tributyrin



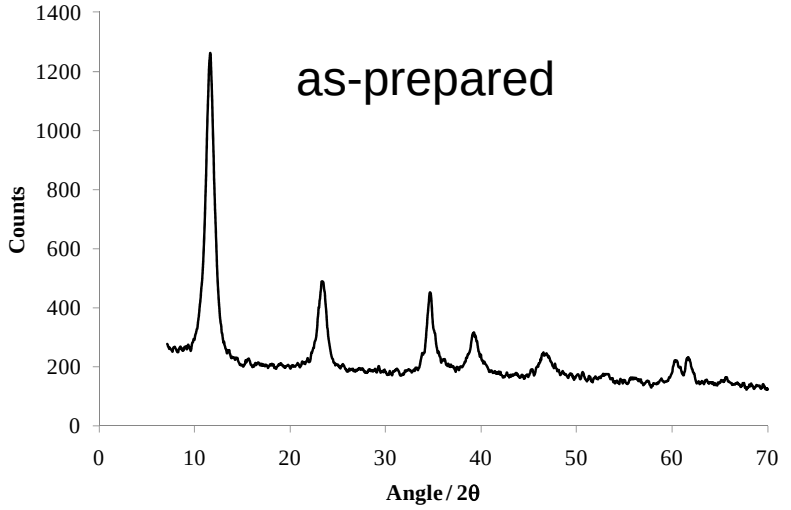
100 g tributyrin,

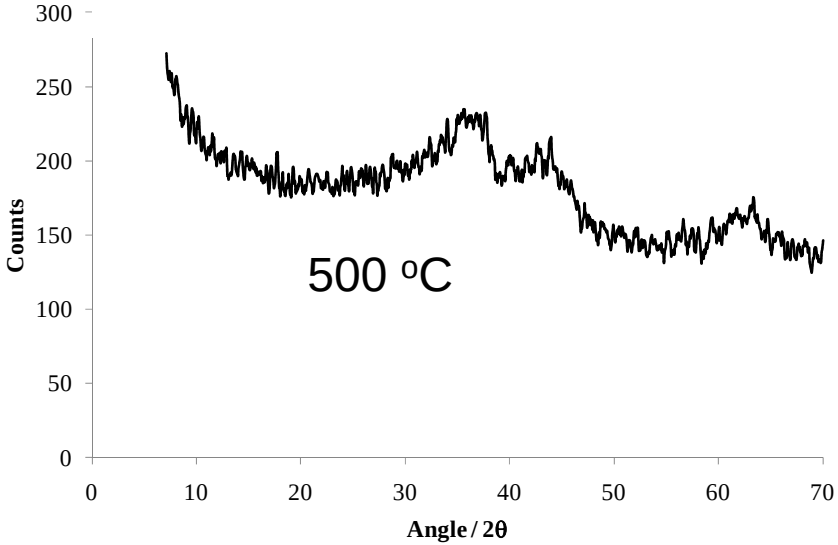
1.6 g catalyst (activated at 150 ^{o}C)

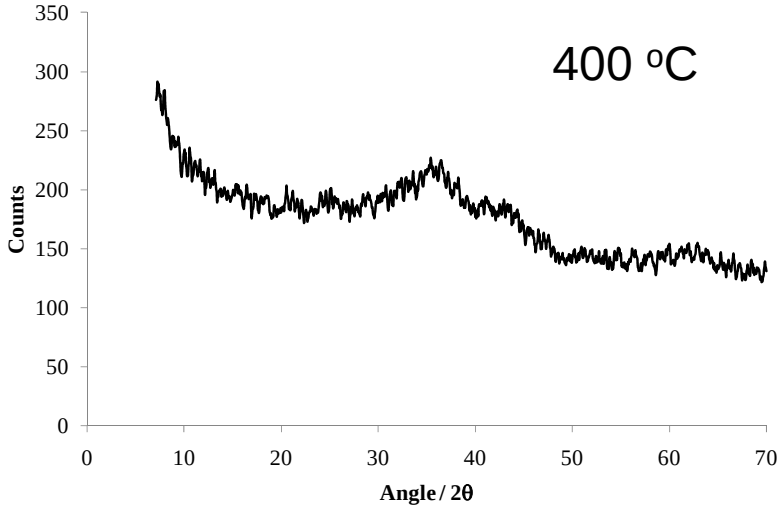
Reaction temperature 60 ^{o}C

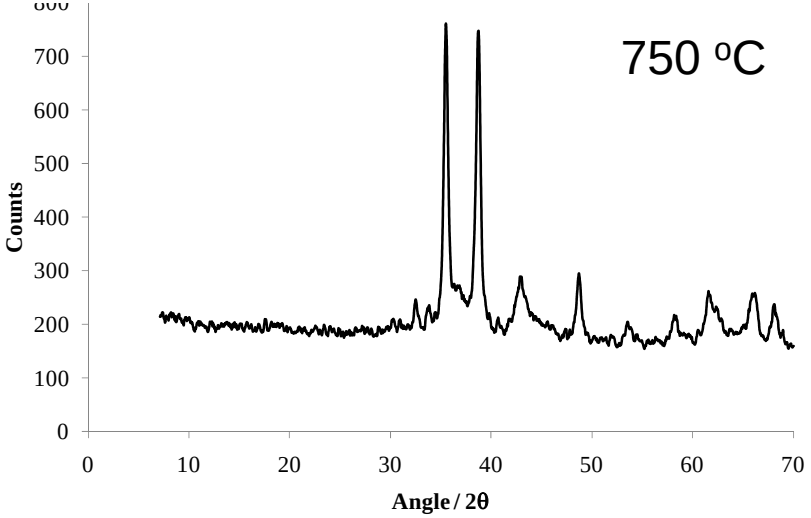
Conversion after 2 hours

$Cu_3Mg_3Al_2(CO_3)(OH)_{16}.4H_2O$ *Conventional heating*









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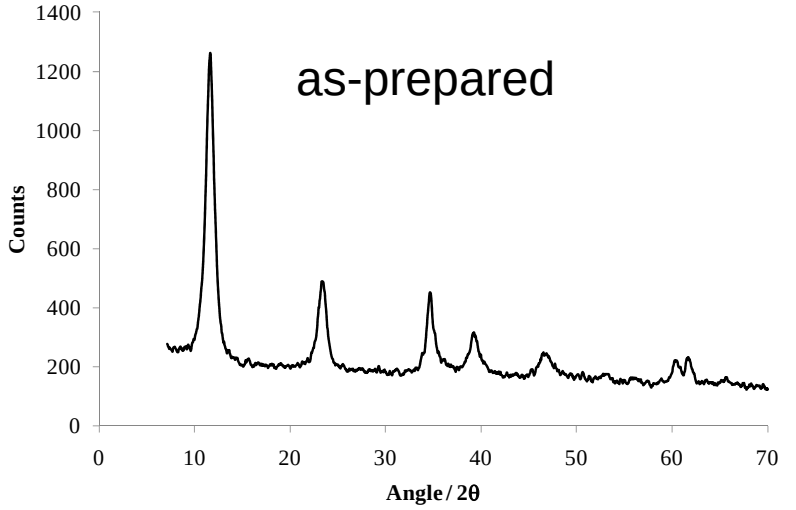

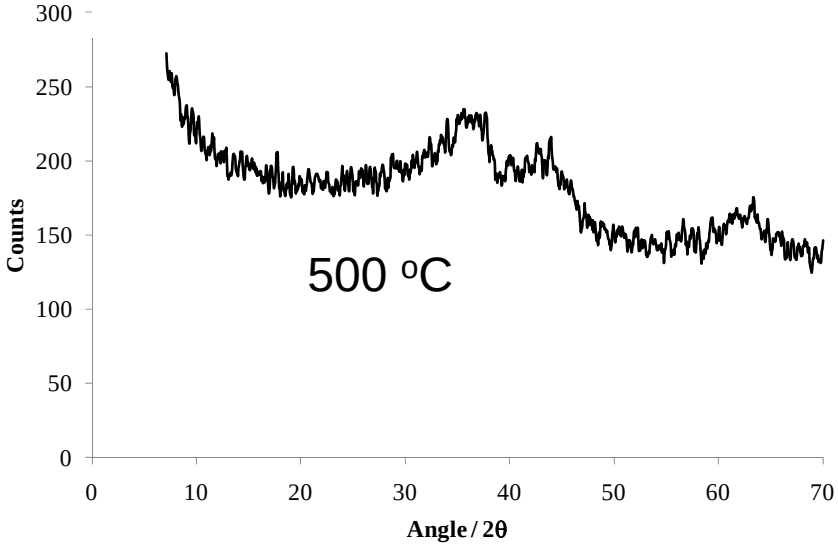

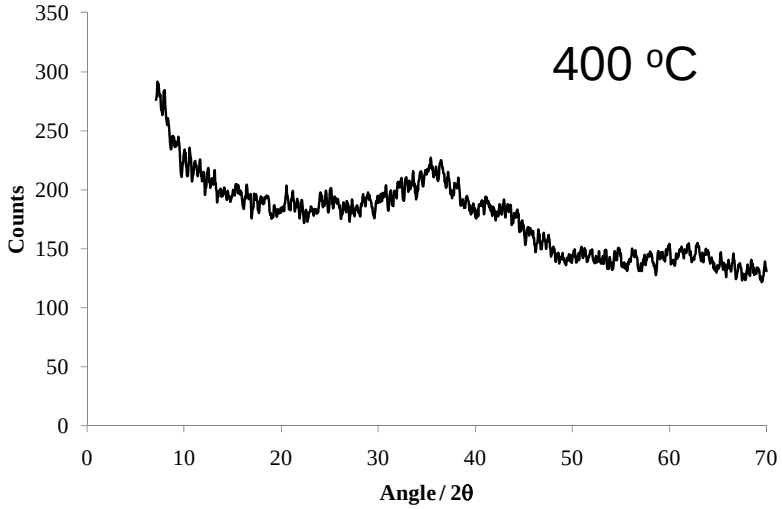

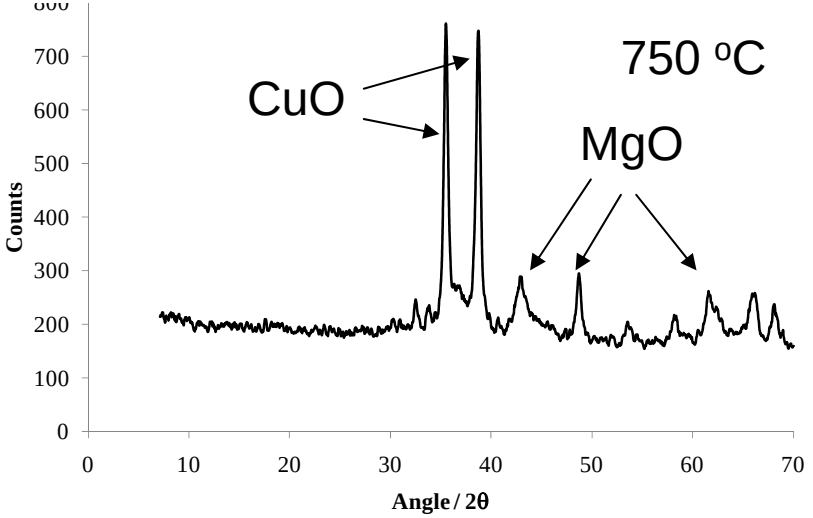

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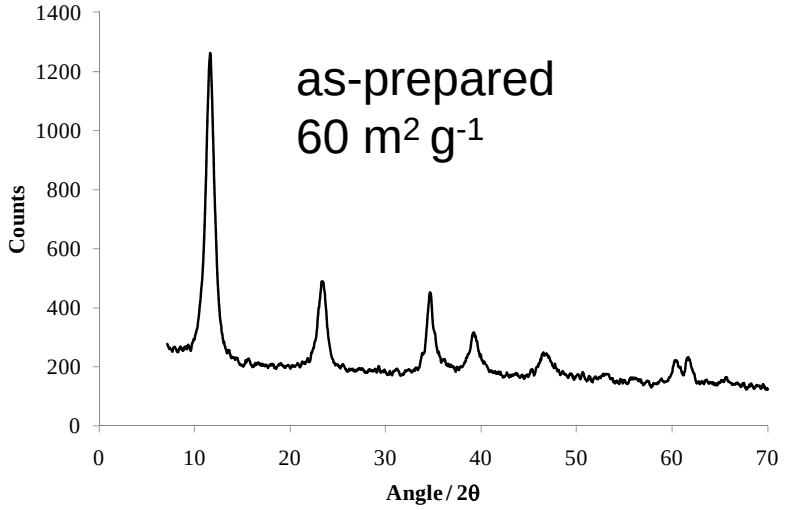

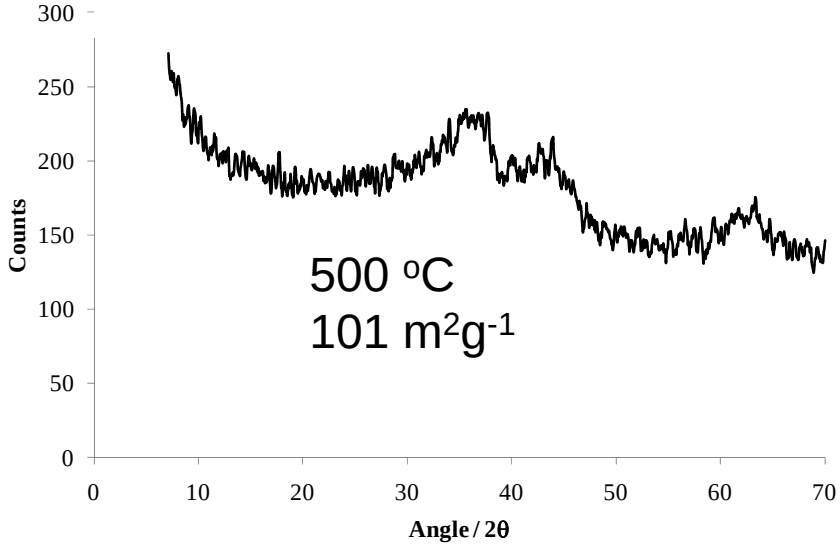

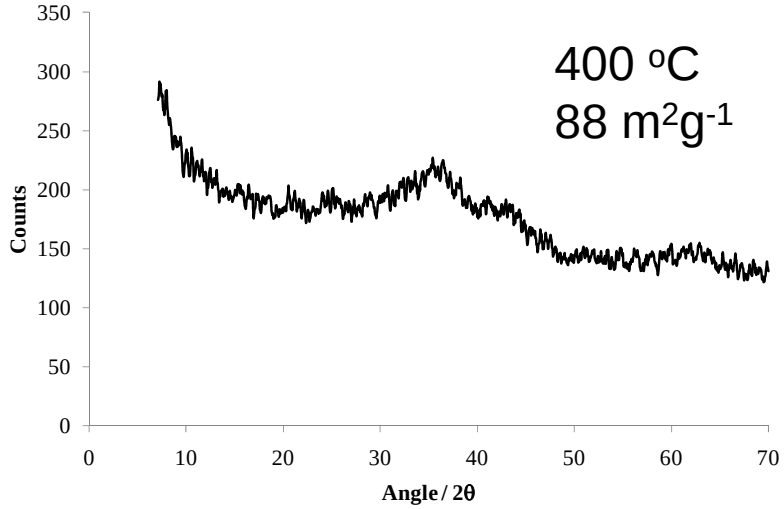

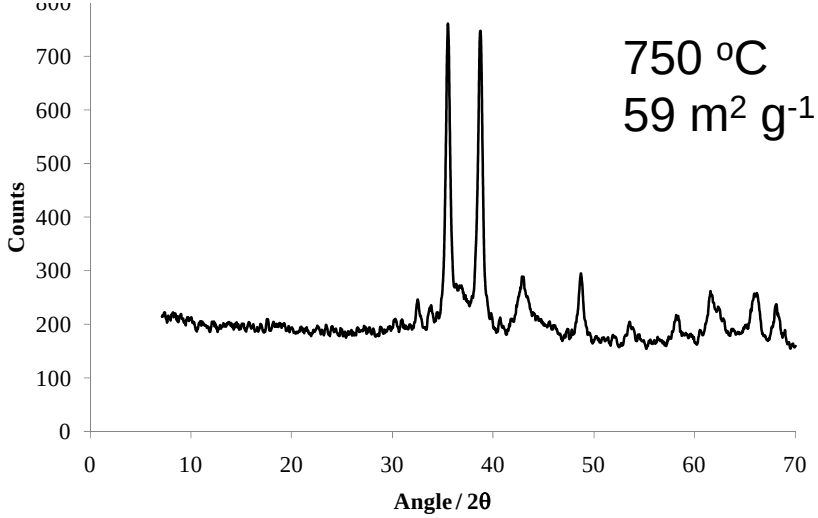

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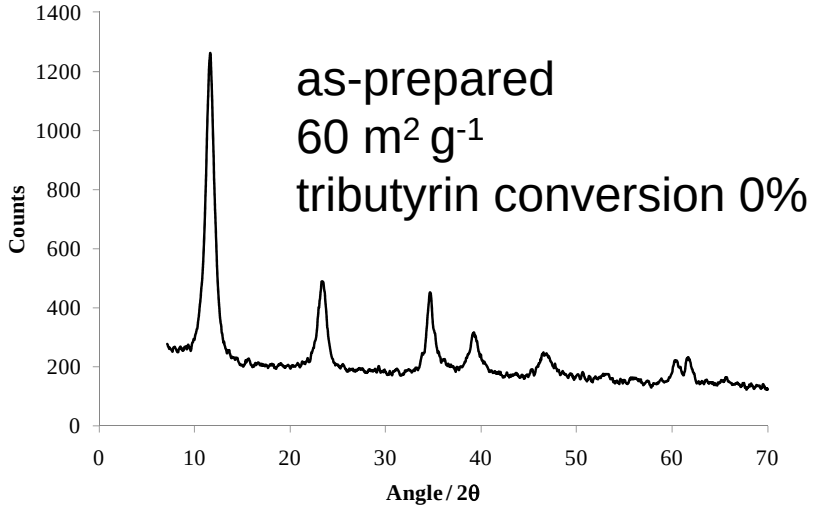
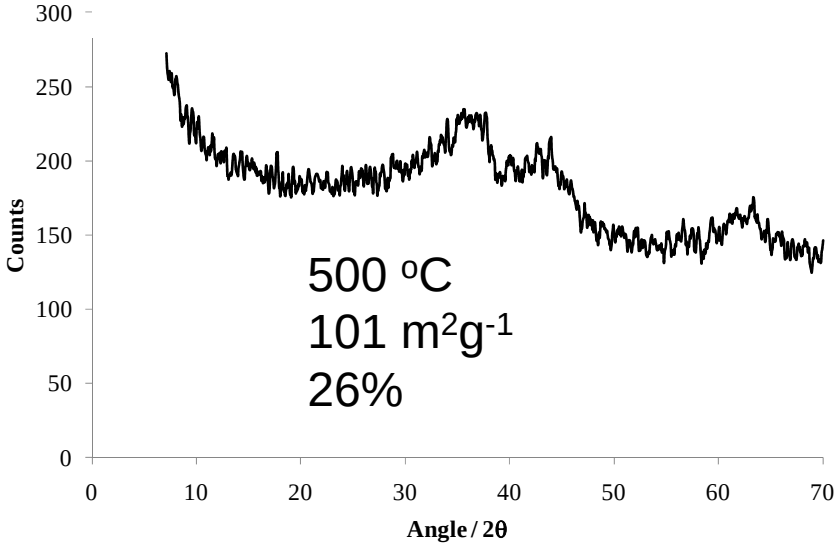
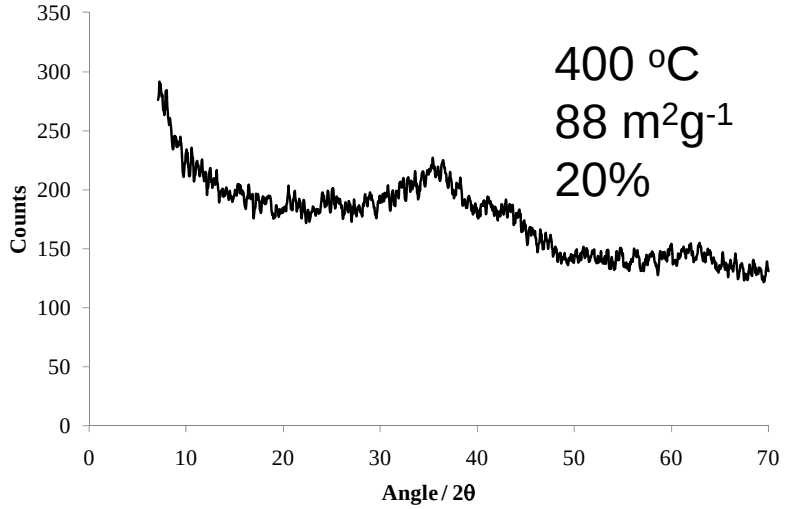
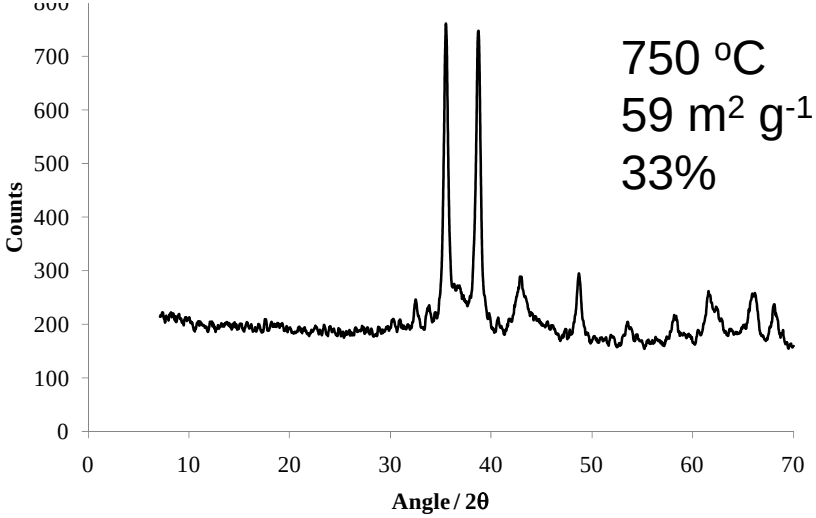




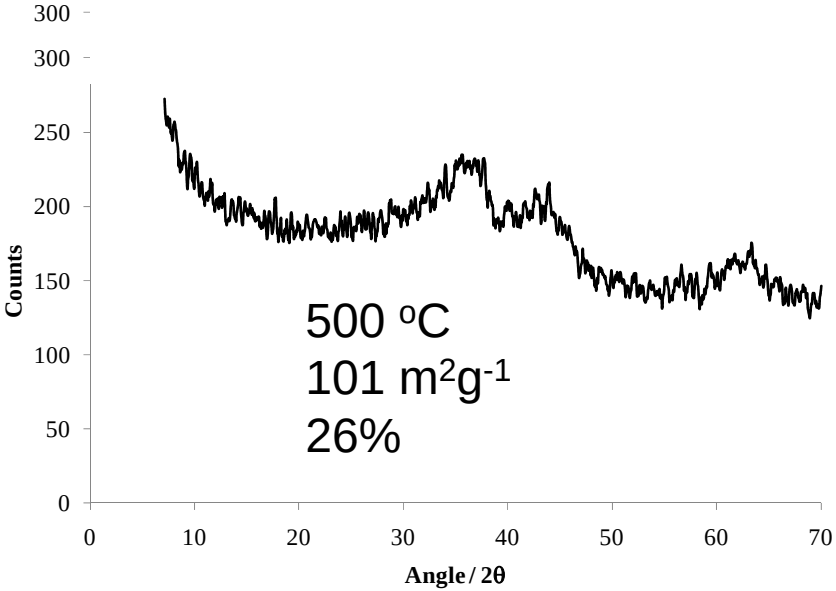


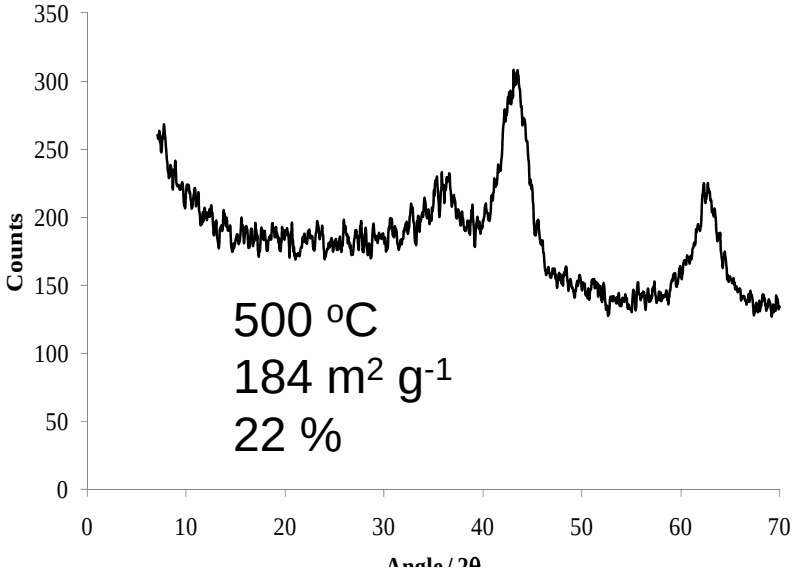


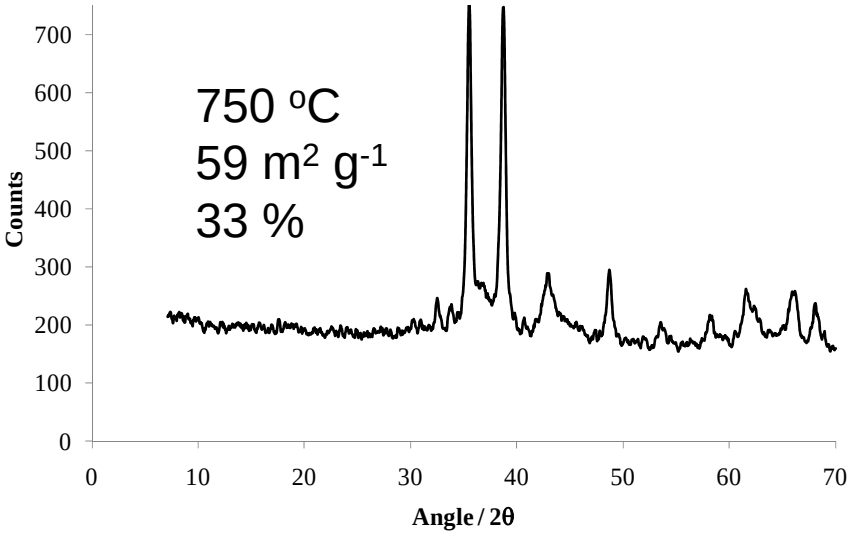
$Cu_3Mg_3Al_2(CO_3)(OH)_{16}.4H_2O$

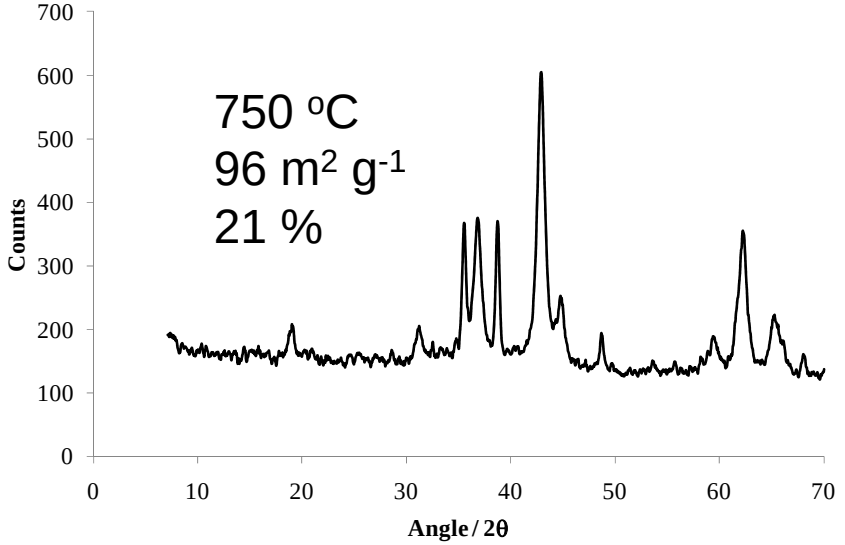
$CuMg_5Al_2(CO_3)(OH)_{16}.4H_2O$

Conventional heating









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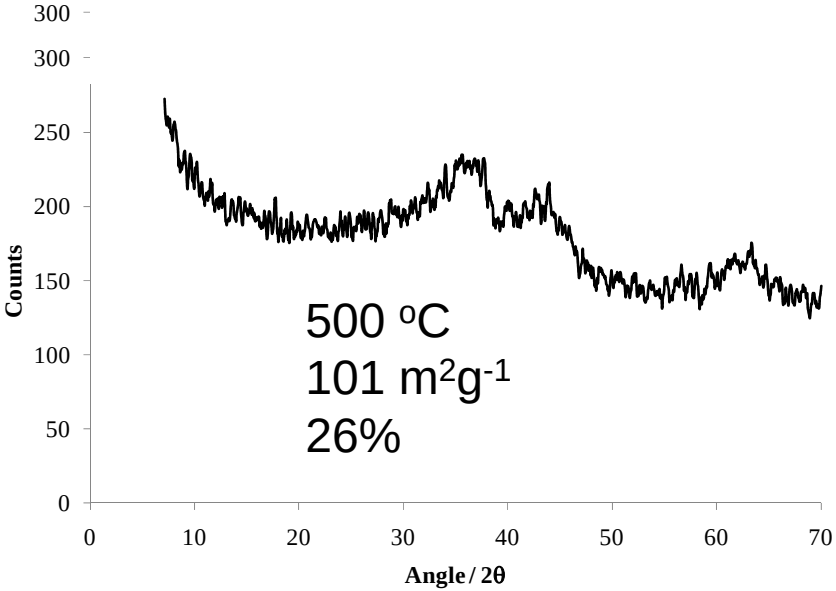
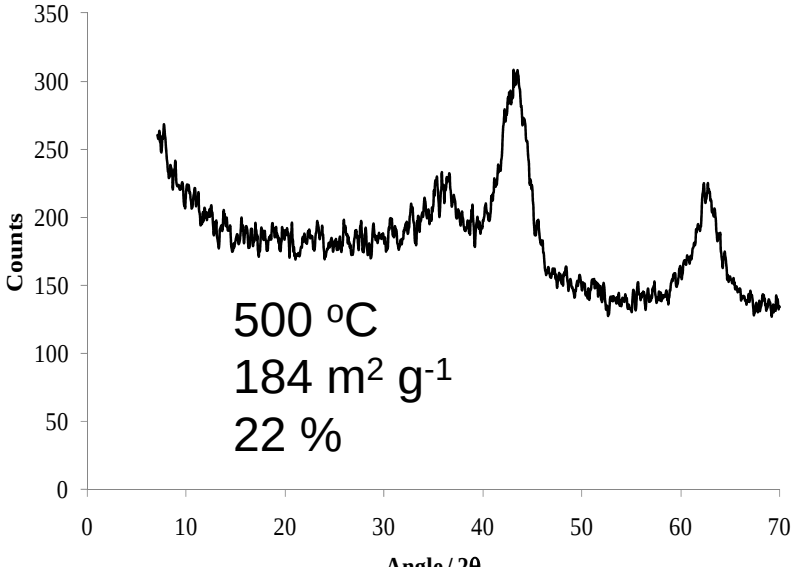
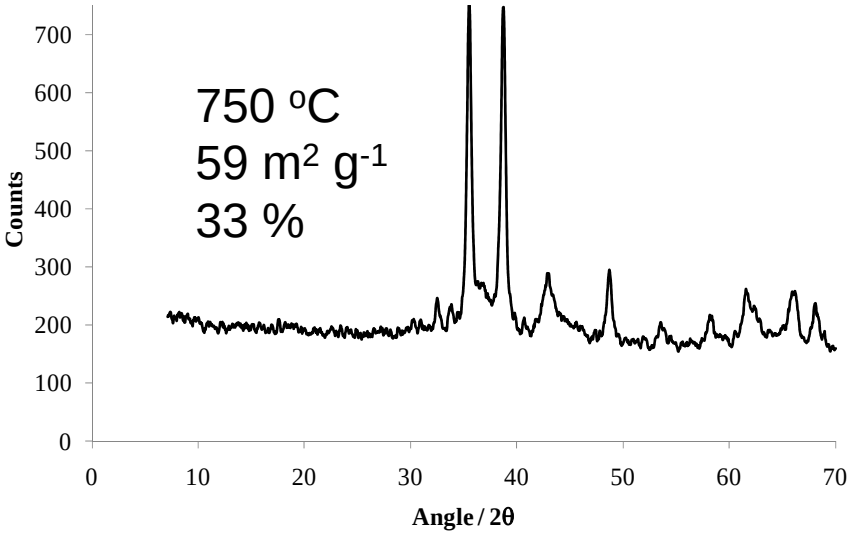
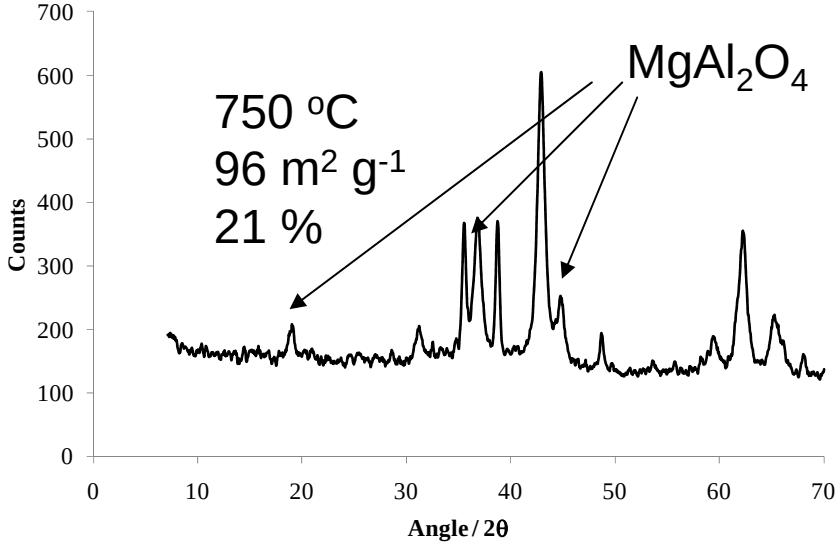








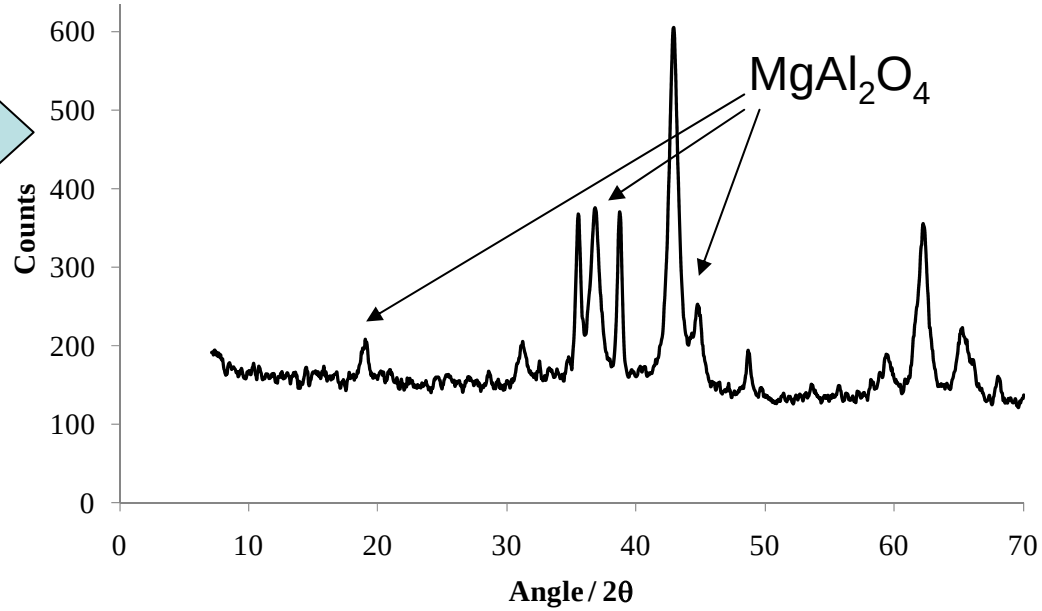
Oxides from LDH's vs mixed pure oxides

$CuMg_5Al_2(CO_3)(OH)_{16}.4H_2O$

calcined at 750 ^oC

96 $m^2\ g^{-1}$

21 % conversion of tributyrin

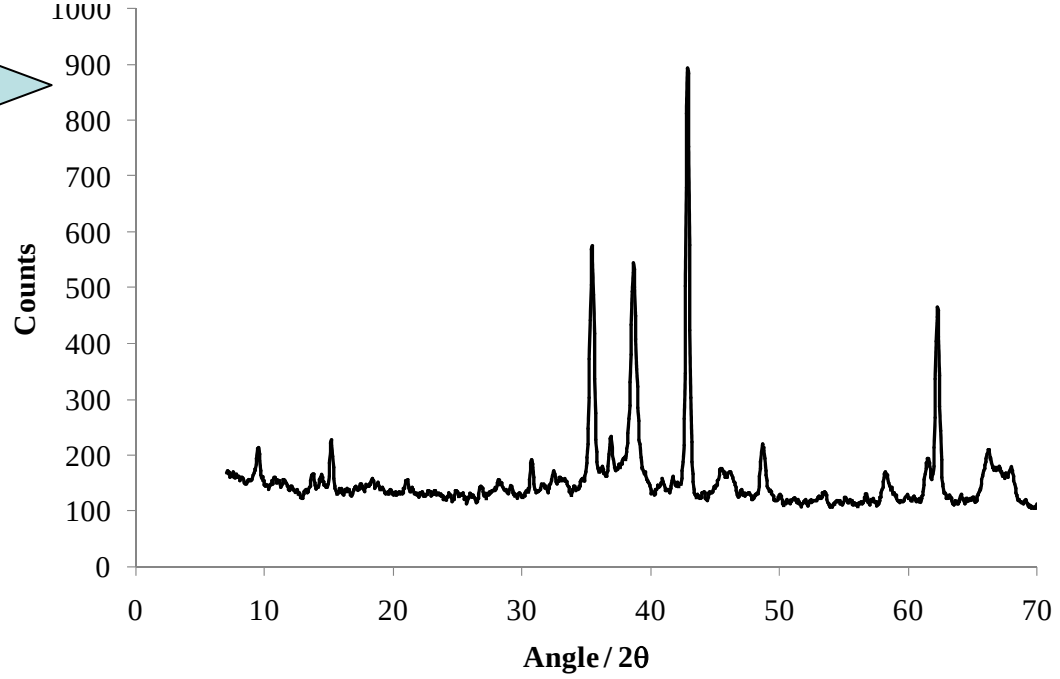


$CuO/MgO/Al_2O_3$

calcined at 750 ^oC

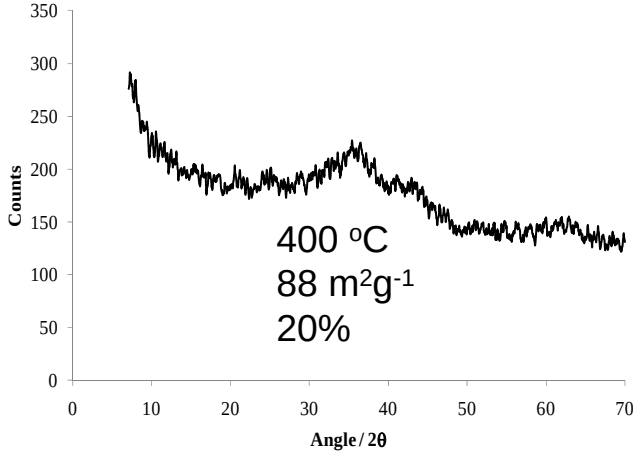
30 $m^2\ g^{-1}$

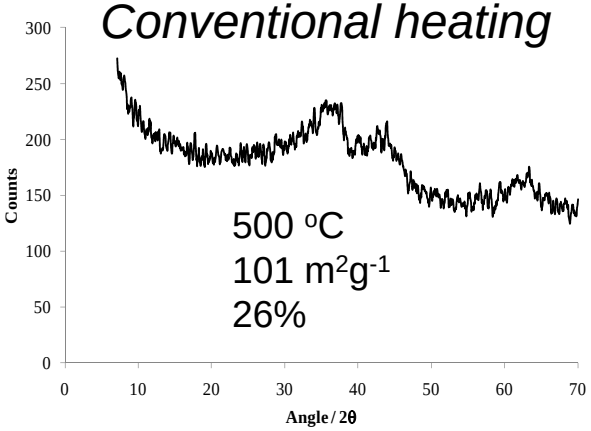
0 % conversion

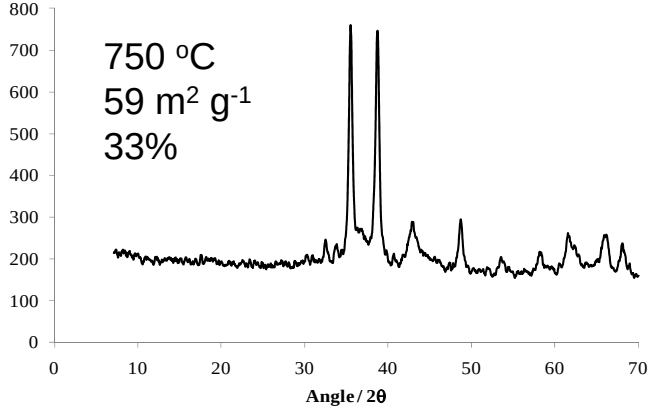


$Cu_3Mg_3Al_2(CO_3)(OH)_{16}.4H_2O$

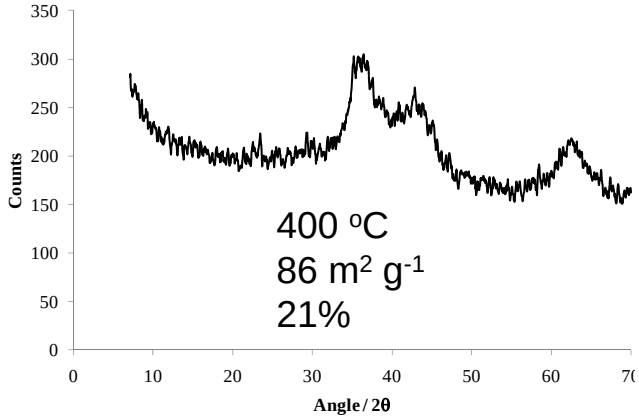
Conventional heating

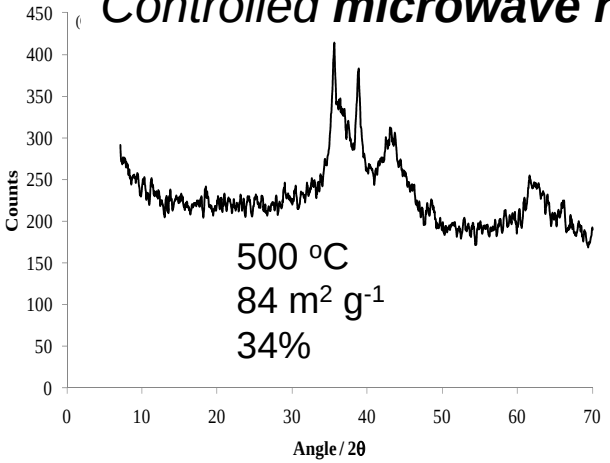


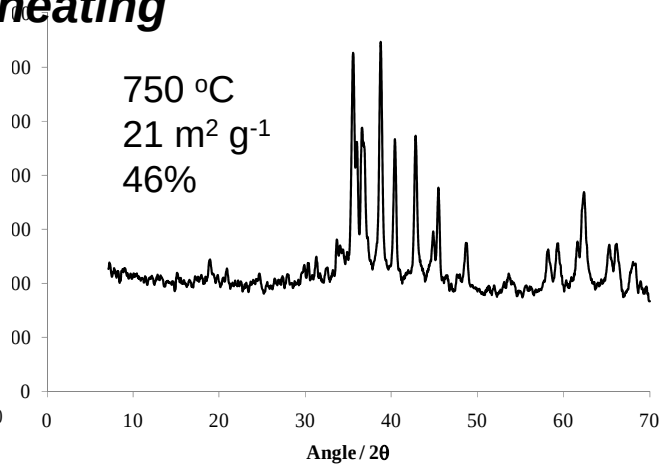




*Controlled **microwave heating***







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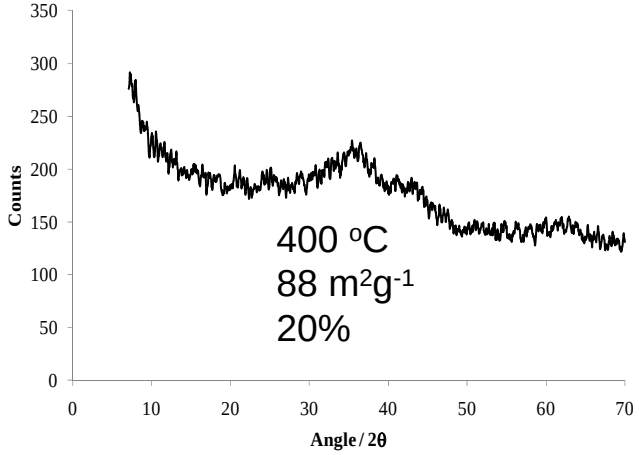
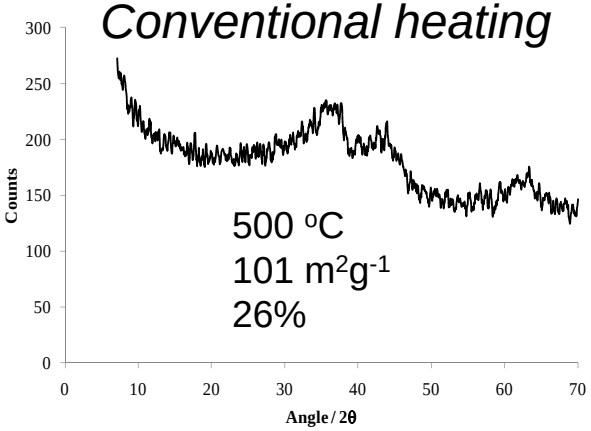
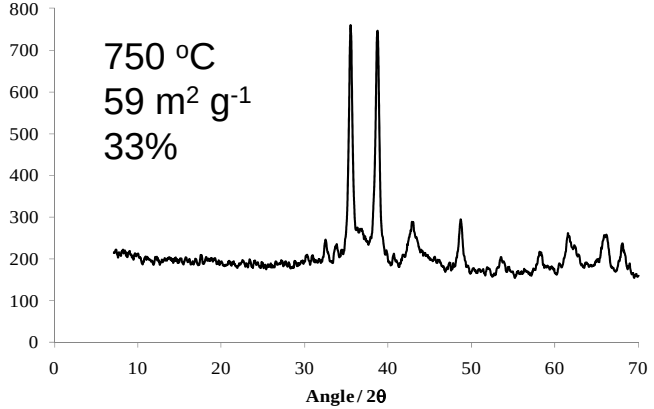
Conventional heating







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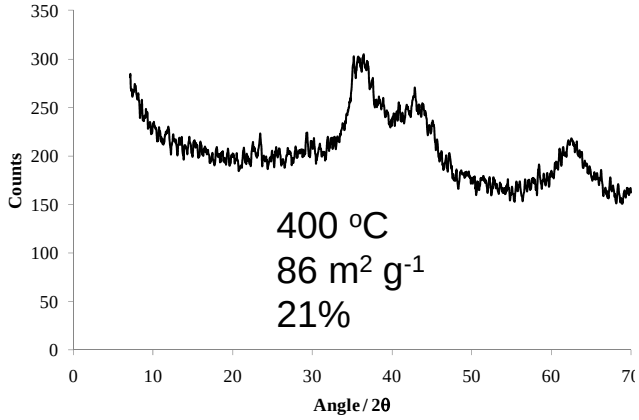
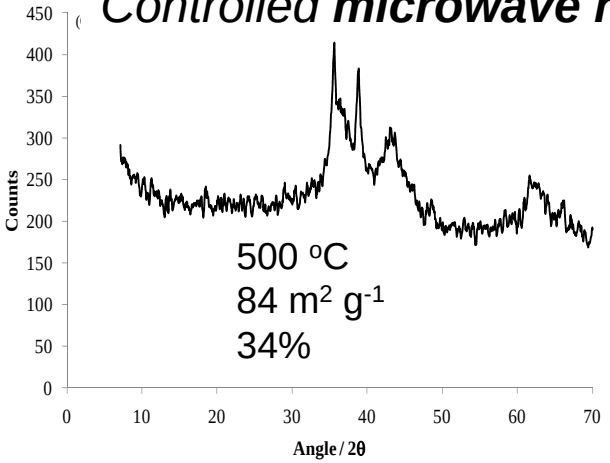
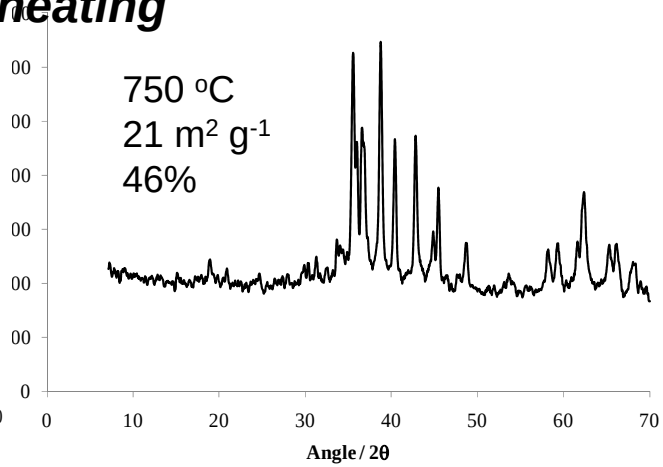


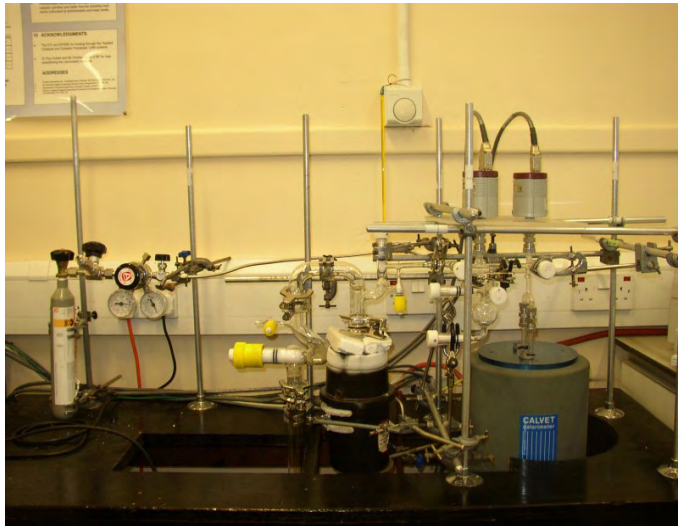


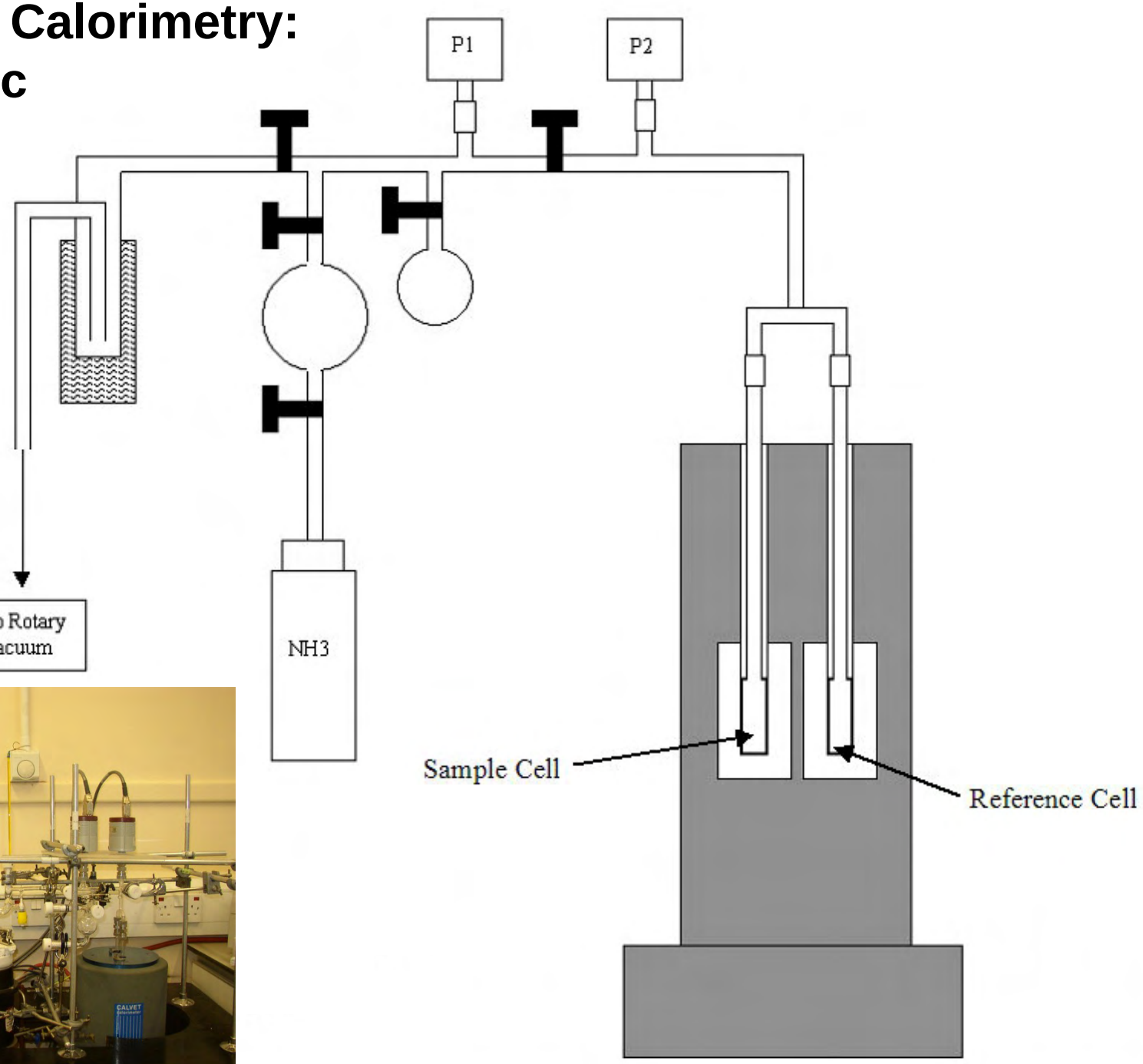


$Cu_3Mg_3Al_2(CO_3)(OH)_{16}.4H_2O$

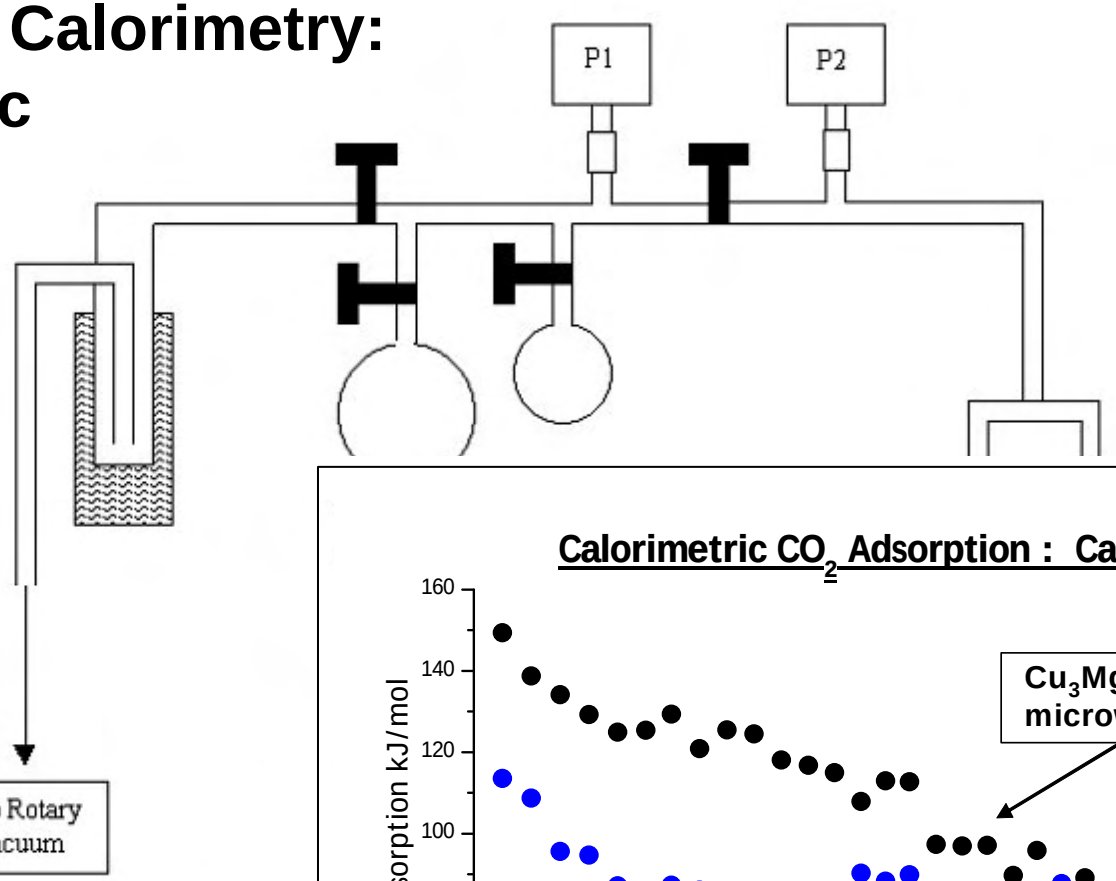
	Conventional heating		***Controlled microwave heating***	
Calcination temperature /^oC	Surface area /$m^2\ g^{-1}$	Catalytic activity – conversion of tributyrin /%	Surface area /$m^2\ g^{-1}$	Catalytic activity – conversion of tributyrin /%
none	60	0	60	0
400	88	20	86	21
500	101	26	84	34
750	59	33	21	46

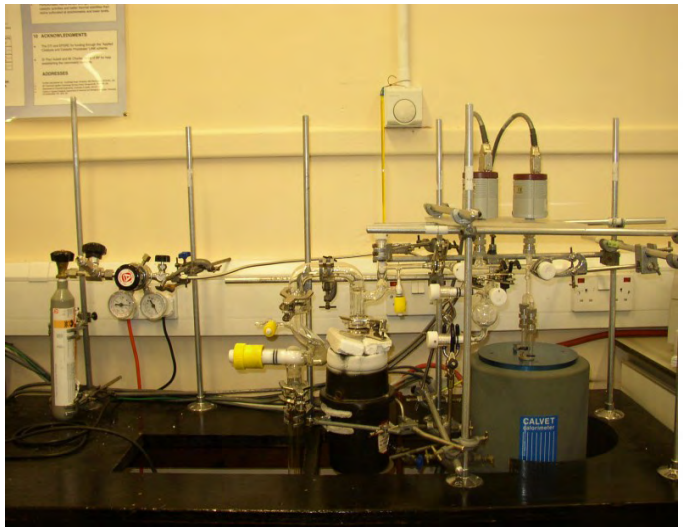
Adsorption Calorimetry: NH_3, CO_2 etc

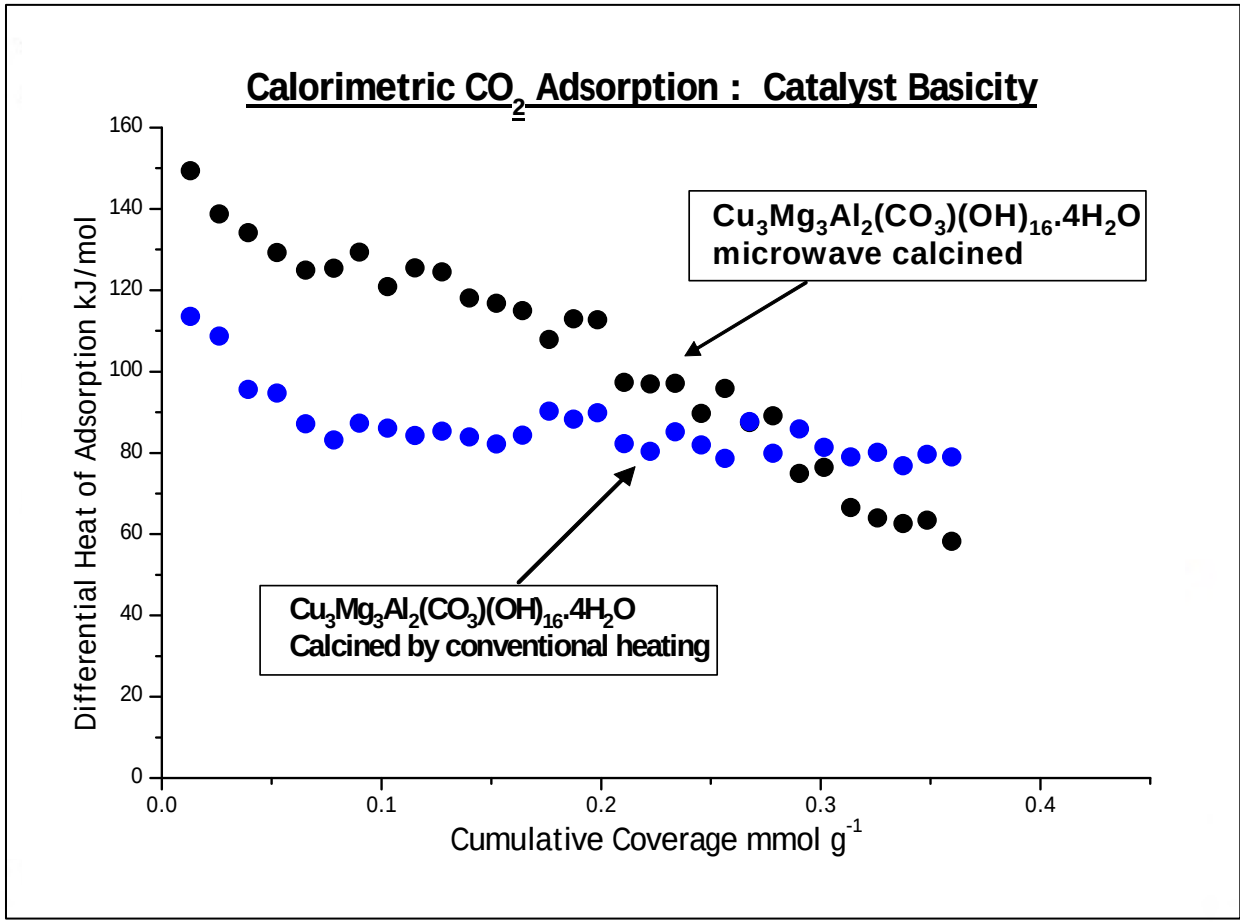




Adsorption Calorimetry: NH_3, CO_2 etc

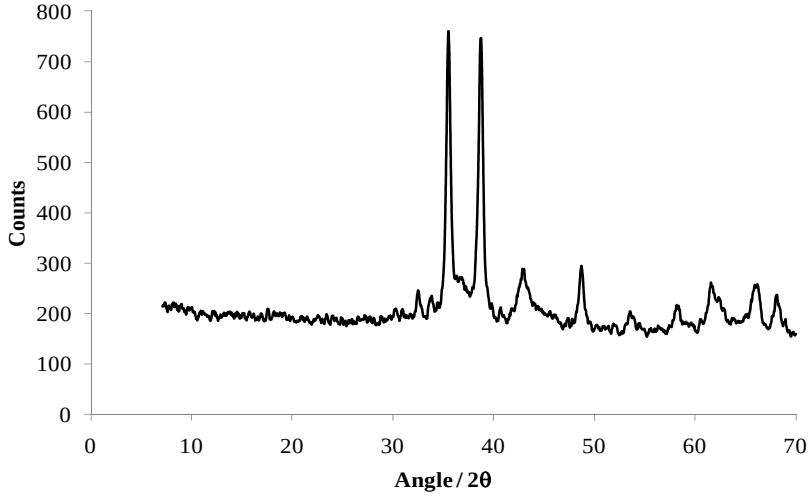




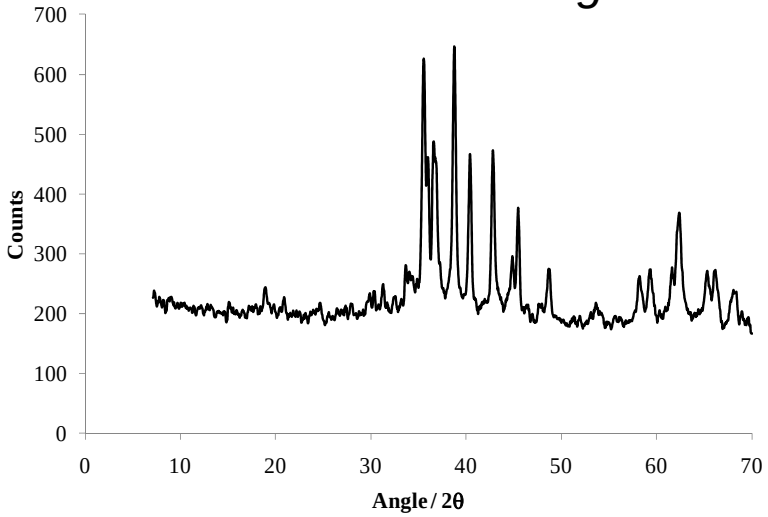


$Cu_3Mg_3Al_2(CO_3)(OH)_{16}.4H_2O$ calcination products

Conventional heating



Microwave heating



Further structural studies:

1 X-ray photoelectron spectroscopy:-
surface species, oxidation numbers

2 Air vs N_2

3 neutron diffraction:-
structural changes in the bulk

Conclusions

In catalyst preparation, using microwave heating for calcination steps is difficult because products often couple with microwaves differently to precursors.

“Controlled” microwave heating ensures temperature control is maintained.

Microwave heating can generate less pronounced temperature gradients in a solid sample than conventional heating.

Microwave calcination can yield different phases to those generated by conventional heating.

In some cases these new phases can exhibit higher catalytic activity than those formed using conventional methods.

Chemistry
/Automotive Engineering

Fuelpod:
Biodiesel production
for engine testing etc