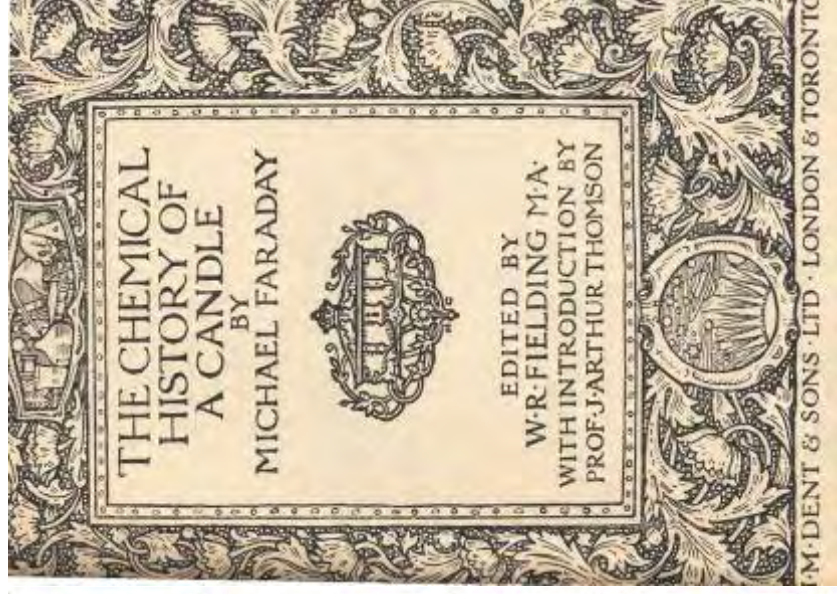


# **Fuels chemistry: history, trends and challenges for alternative fuels**

**John Griffiths  
School of Chemistry,  
The University,  
Leeds LS2 9JT**

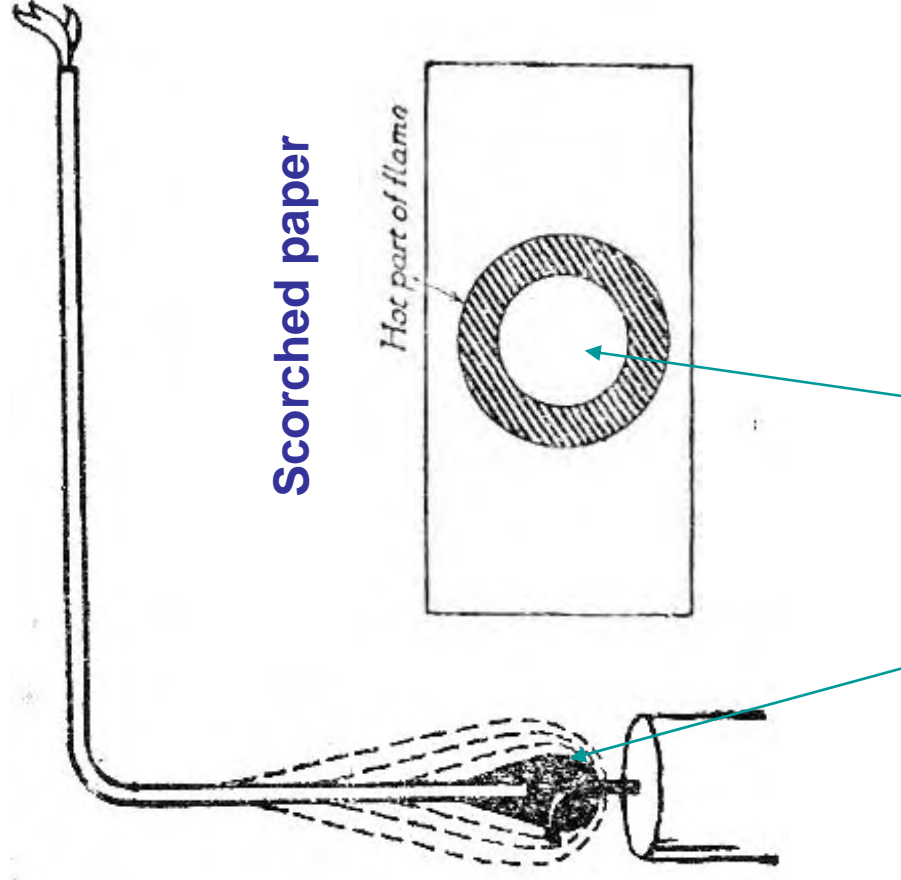
# 1. HISTORY

- focus on combustion chemistry

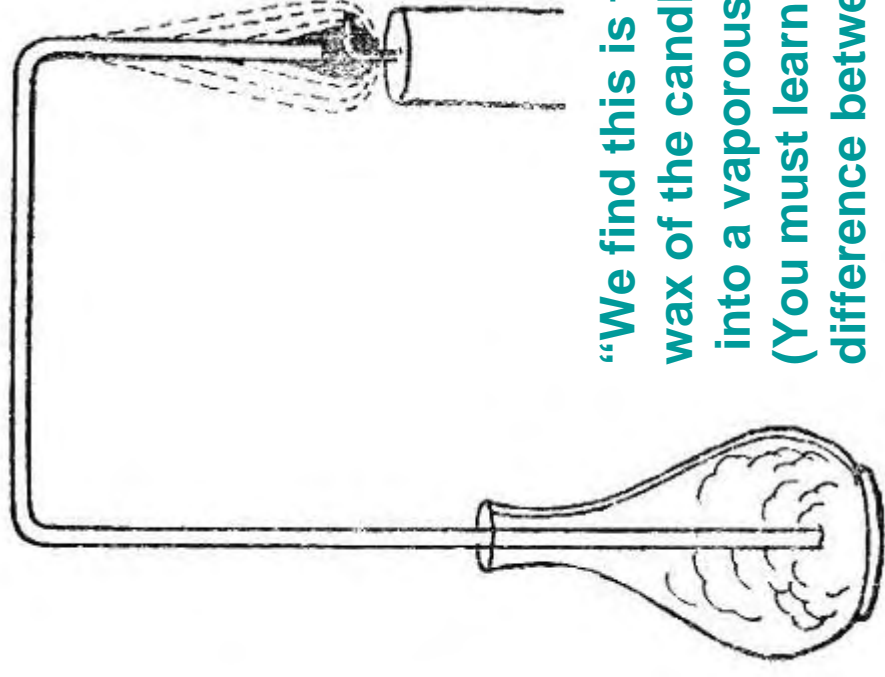


Faraday's lectures circa 1850 (1920s edition)

# Faraday's experiments on a diffusion flame



Flammable vapours formed  
In the “anaerobic” centre of flame



“We find this is the  
wax of the candle made  
into a vaporous liquid.  
(You must learn the  
difference between a  
gas and vapour...”

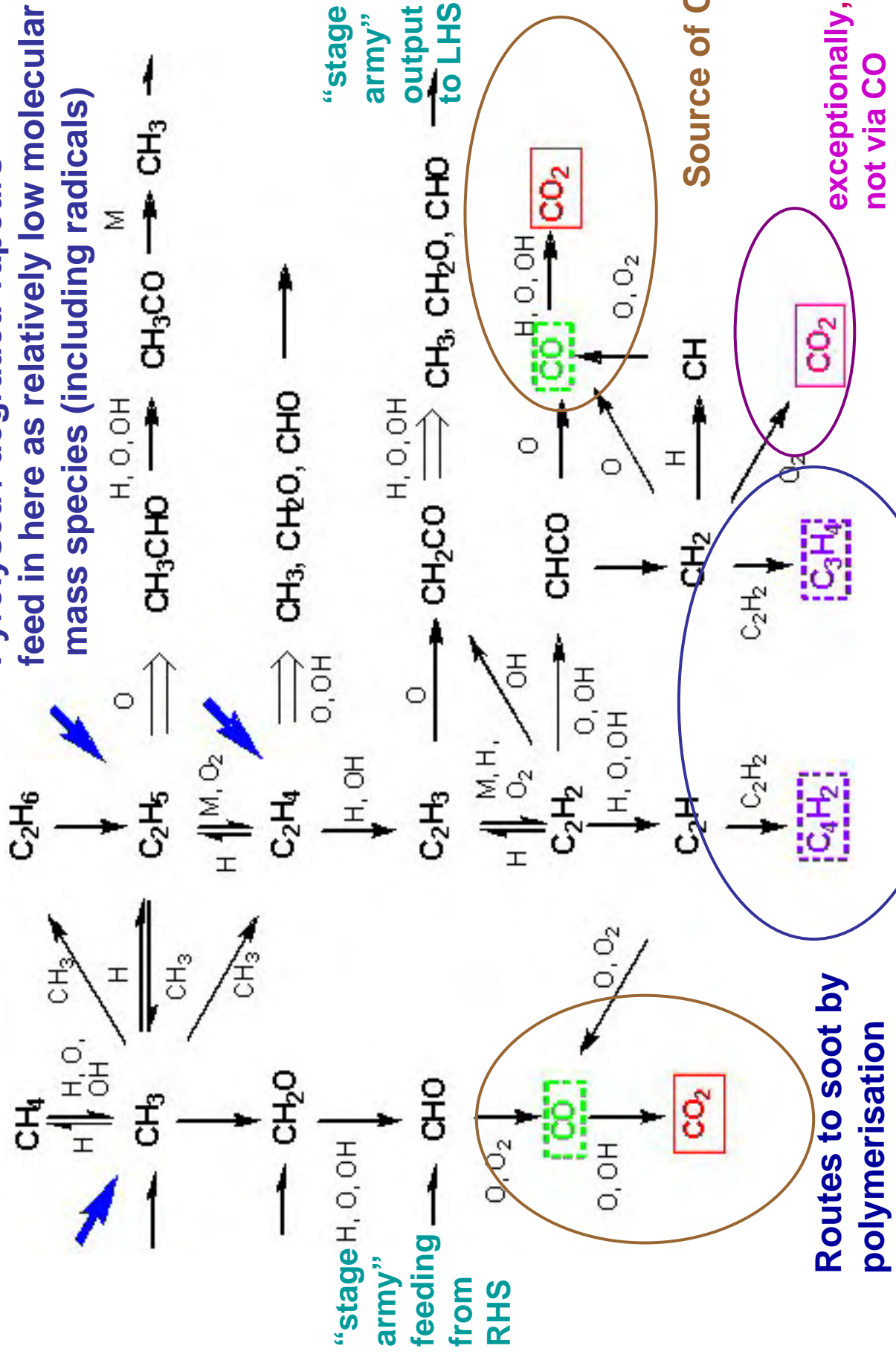
i.e. not the highly condensable  
 $C_{30}$  - or so - of candle wax but  
of lower molecular mass

# Modern chemical interpretations (after 1980)

(after Warnatz, Pure and Applied Chem 72, 2101, 2000)

## Pyrolysed / degraded vapours

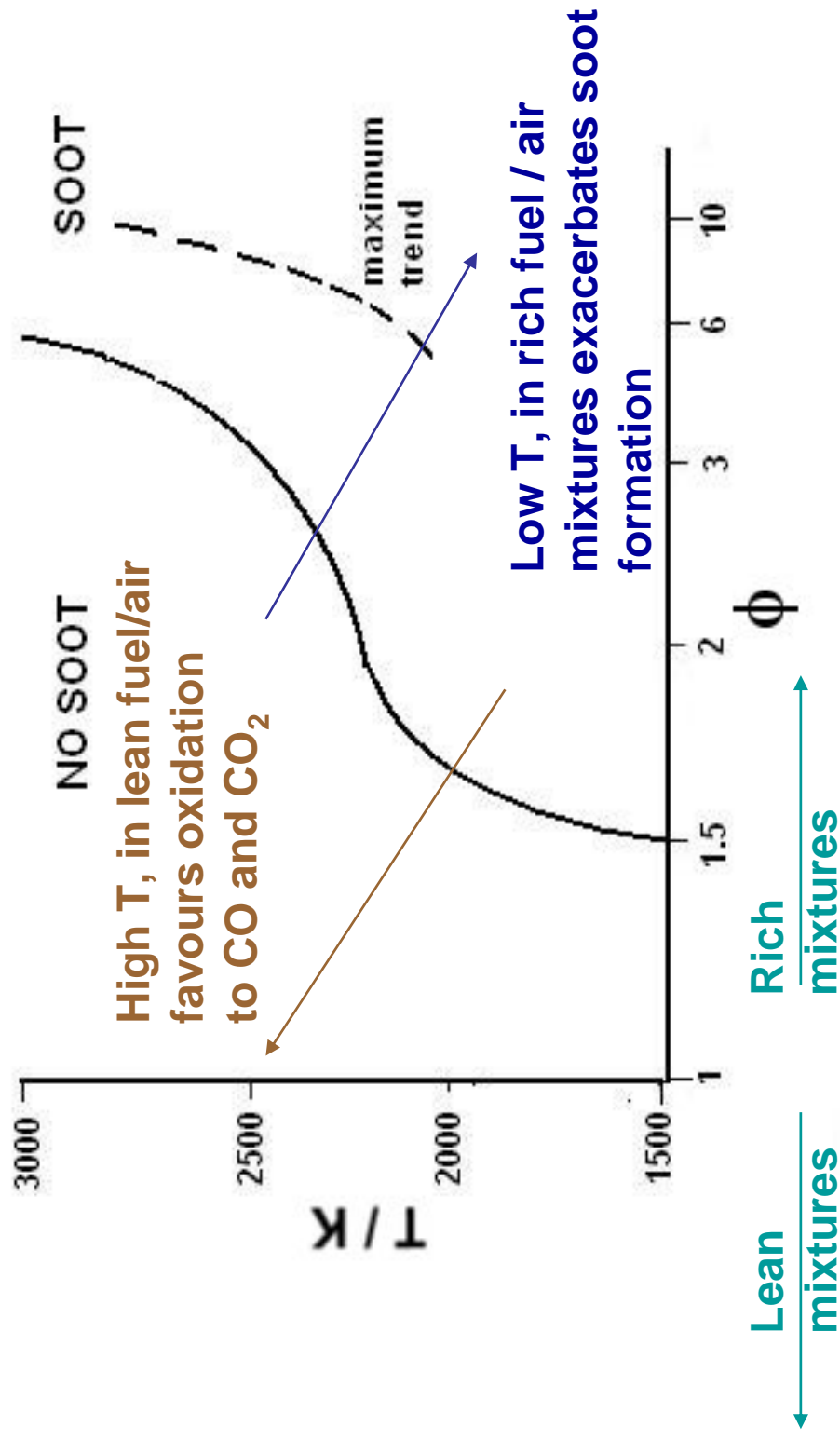
feed in here as relatively low molecular mass species (including radicals)



## POLLUTANT FORMATION:

### Regimes for soot formation in premixed conditions

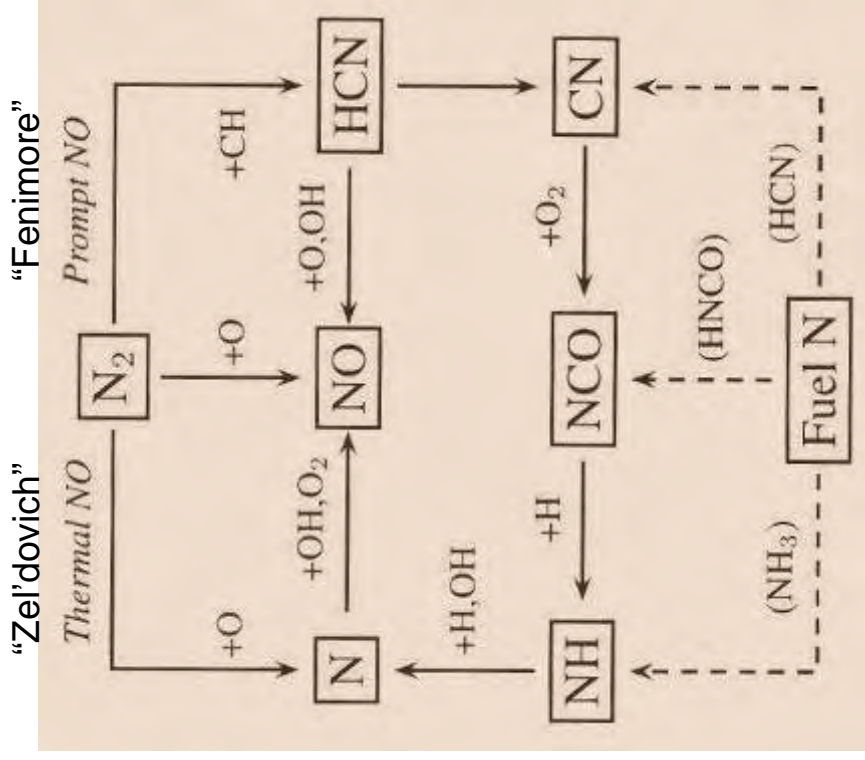
(after Homann, Comb. Sci. Tech., 33, 1, 1983)





# POLLUTANT FORMATION: Reactions of the free radical pool in flames involving and leading to $\text{NO}_x$ and $\text{SO}_x$

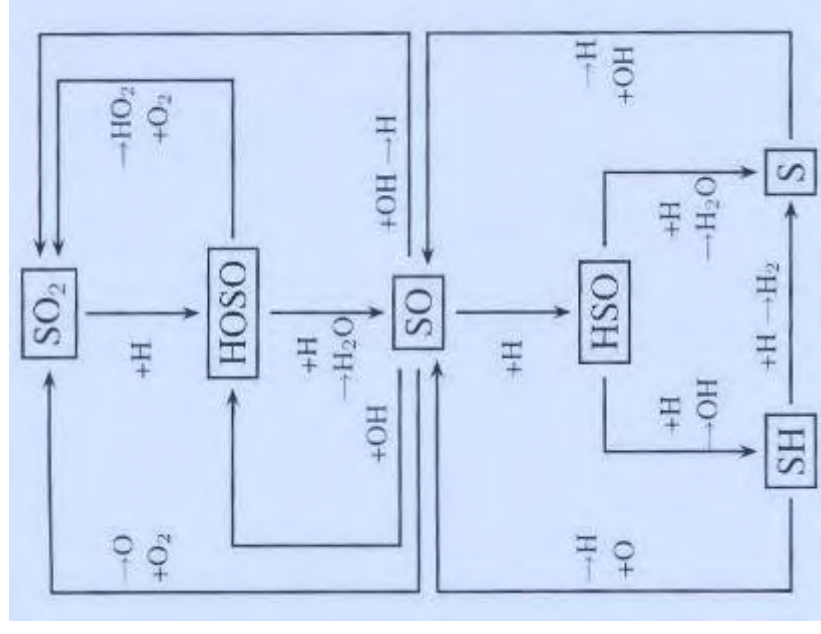
## Atmospheric N



## Fuel-bound N

The main volatile from biomass is  $\text{NH}_3$ .  
From coal it is HCN.

## Pathways of S-containing fragments in fuel-rich conditions



Fuel-bound S is largely released in the gas-phase as  $\text{H}_2\text{S}$  or organo-sulphur compounds

## 2. TRENDS (and DILEMMAS?)

### - focus on fuel development / usage



#### Drax Power Station, Yorkshire



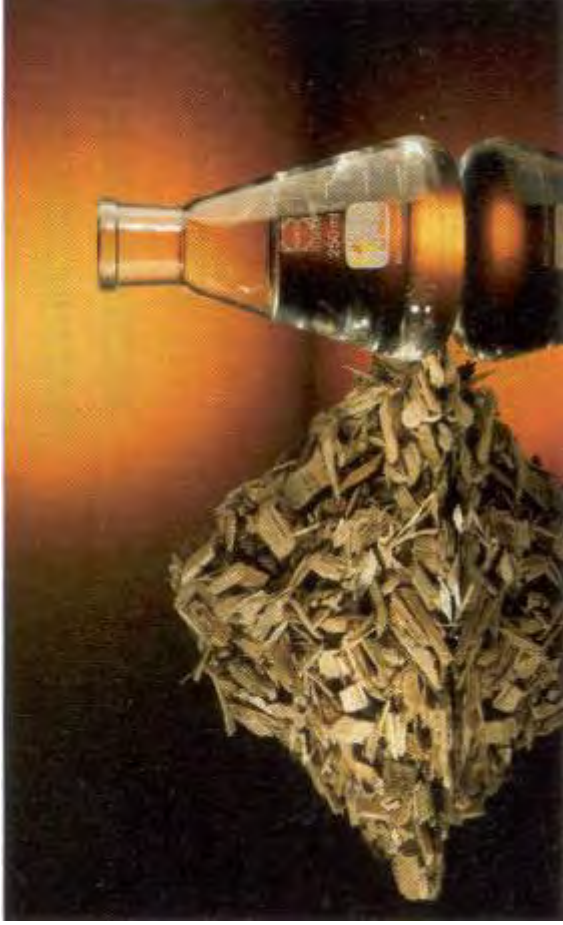
- Largest, cleanest and most efficient coal-fired power station in the UK
- Six 660MW units, giving a total capacity of 4,000MW
- Current output level around 24TWh pa, some 7% of the UK's electricity needs
- Pulverised coal firing
- Coal and alternative fuel burn between 9 to 10 million tonnes pa
- Drax is already capable of firing 5,000 tonnes/wk of solid biomass

Land usage –  
for animal / human foodstock  
or biomass feedstock?

Courtesy of Dr Nigel Burnett, Drax Power Ltd.

# BIOMASS (and ANOTHER DILEMMA?)

**‘Biomass’**: the biodegradable fraction of products, waste and residues from agriculture (including vegetable and animal substances), forestry and related industries, as well as the biodegradable fraction of industrial and municipal waste.



“Chemistry World”, July 2007, by permission

**Should biomass be used directly, as at Drax, or processed to high grade, liquid fuels?**



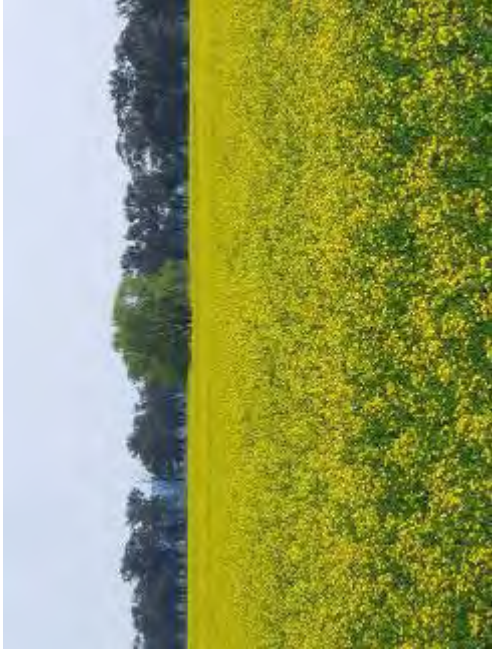
# TRANSPORTATION FUELS - petrol

Biomass, such as sugar cane/beet or maize is turned into ethanol, to be blended in petrol



Ethanol also has the potential for etherification to ethyl-t-butyl ether - which has lower volatility and excellent combustion characteristics in petrol

# TRANSPORTATION FUELS - diesel



“Biodiesel” (from base catalysed transesterification of triglycerides) refers to mono alkyl esters of long chain fatty acids derived from natural oils. In the EU rapeseed methyl ester (RME) is blended into diesel.

5% RME can be incorporated in diesel fuel without need for engine modification.

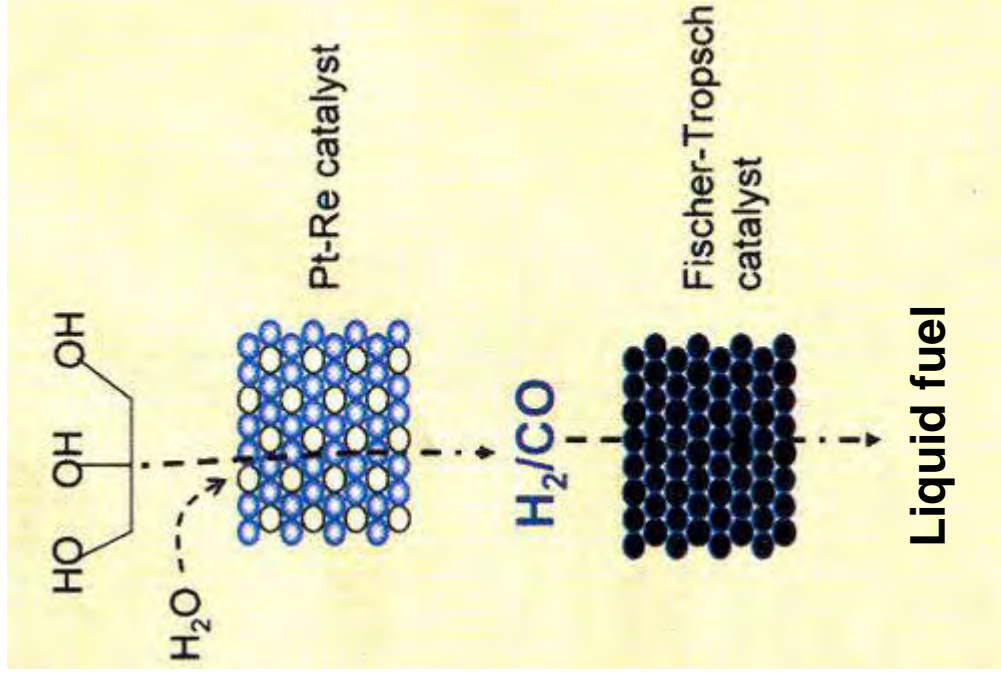
“D1 Oils Establishes Biodiesel Refinery Site on Teesside”



- Requires dedicated land for feedstock
- Potential snags of ash residues and metal content (K, P, Na)



# PRODUCTION DEVELOPMENTS - 1



Synthesis gas ( $H_2$  /  $CO$ ) can be made from glycerol (or other biomass derivatives) and then converted to alkanes

Originating from the 1920s, the F-T process catalysts are based on Fe or Co.

An example of the stoichiometry is:

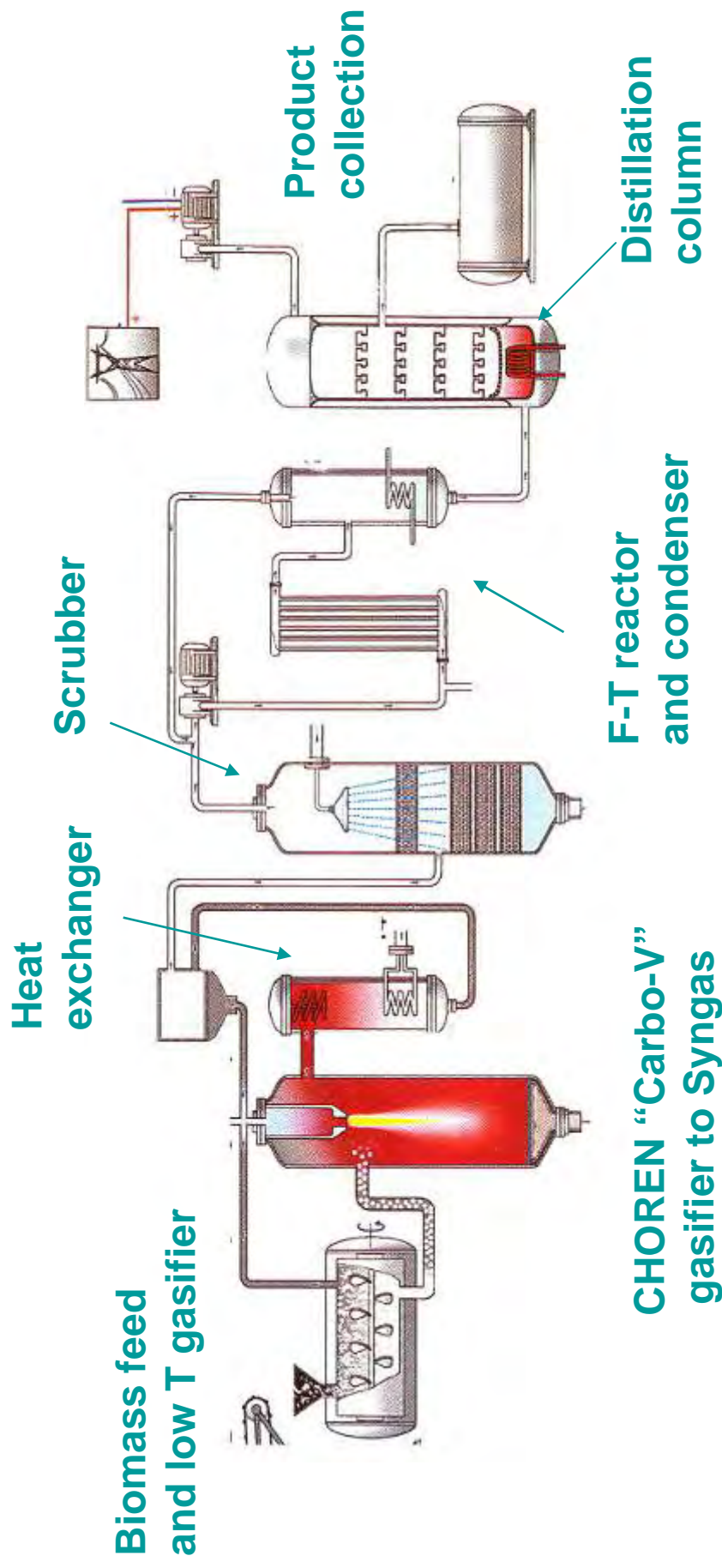


An example developed by “Choren” using glycerol as the fuel



# PRODUCTION DEVELOPMENTS – 2

## Biomass to liquid fuels – “Sunfuel” method

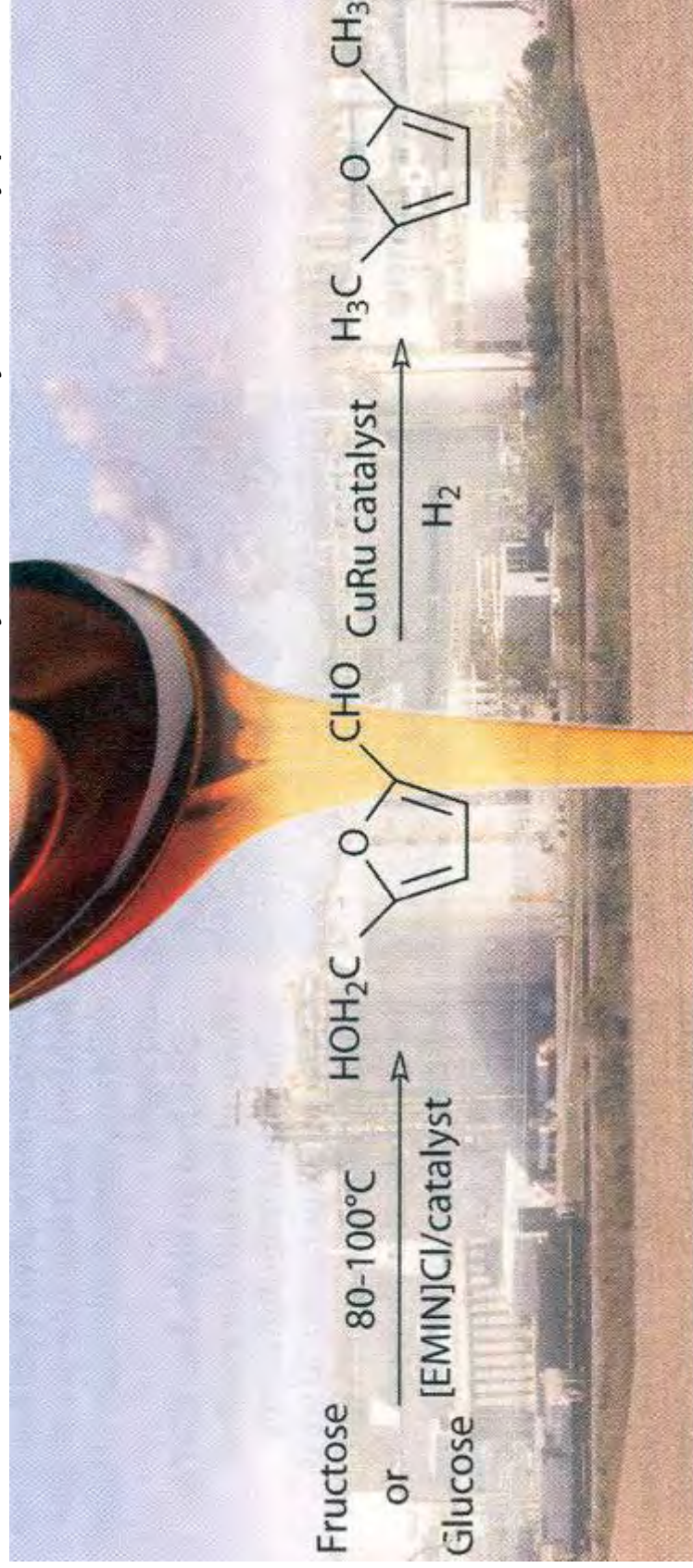


The Fischer-Tropsch (F-T) process is virtually always preceded by gasification, i.e., heating the fuel to generate Syngas ( $H_2$  / CO) without causing complete combustion. This requires a renewables energy source if it is to confer a favourable  $CO_2$  balance overall .



# PRODUCTION DEVELOPMENTS - 3

“Chemistry World”, July 2007, by permission



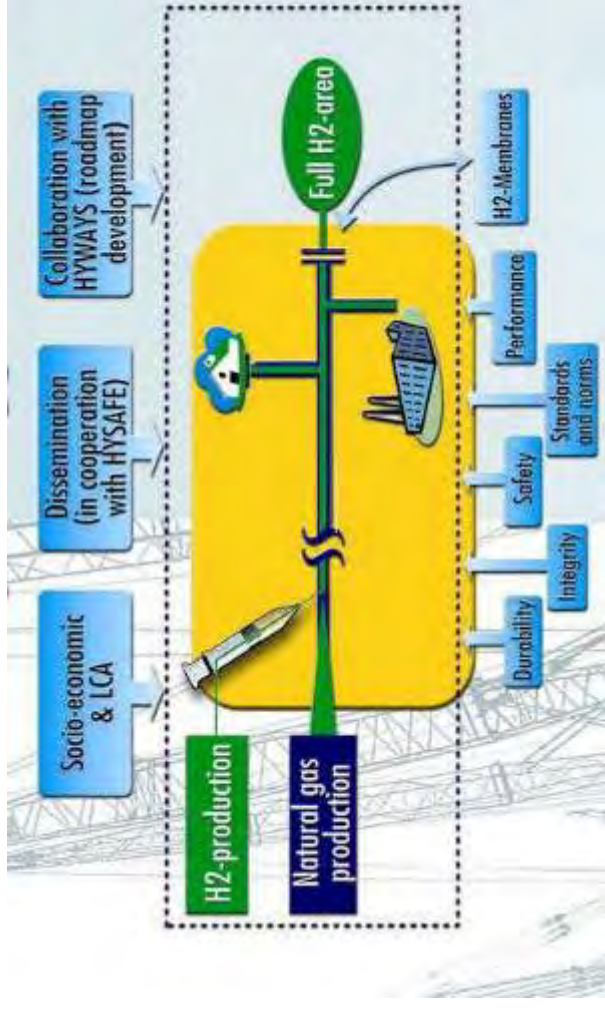
**From sugars to 2,5-dimethylfuran via 5-hydroxymethylfurfural**

**This product is a potential intermediate for plastics production and as a component to add to petrol**

# NATURAL GAS AND THE HYDROGEN ECONOMY



## Using the existing natural gas system for hydrogen



The conditions under which hydrogen can be added to natural gas in the existing system are being addressed. (The physical and chemical properties are affected.)

### Principal issues:

- Safety
- Pipeline durability and integrity
- Appliance performance
- Socio-economic and life-cycle analysis

# 3 CHEMISTRY RELATED CHALLENGES

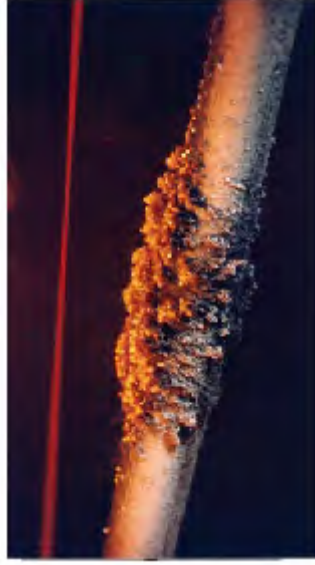
## - Cofiring biomass

### Incentives:

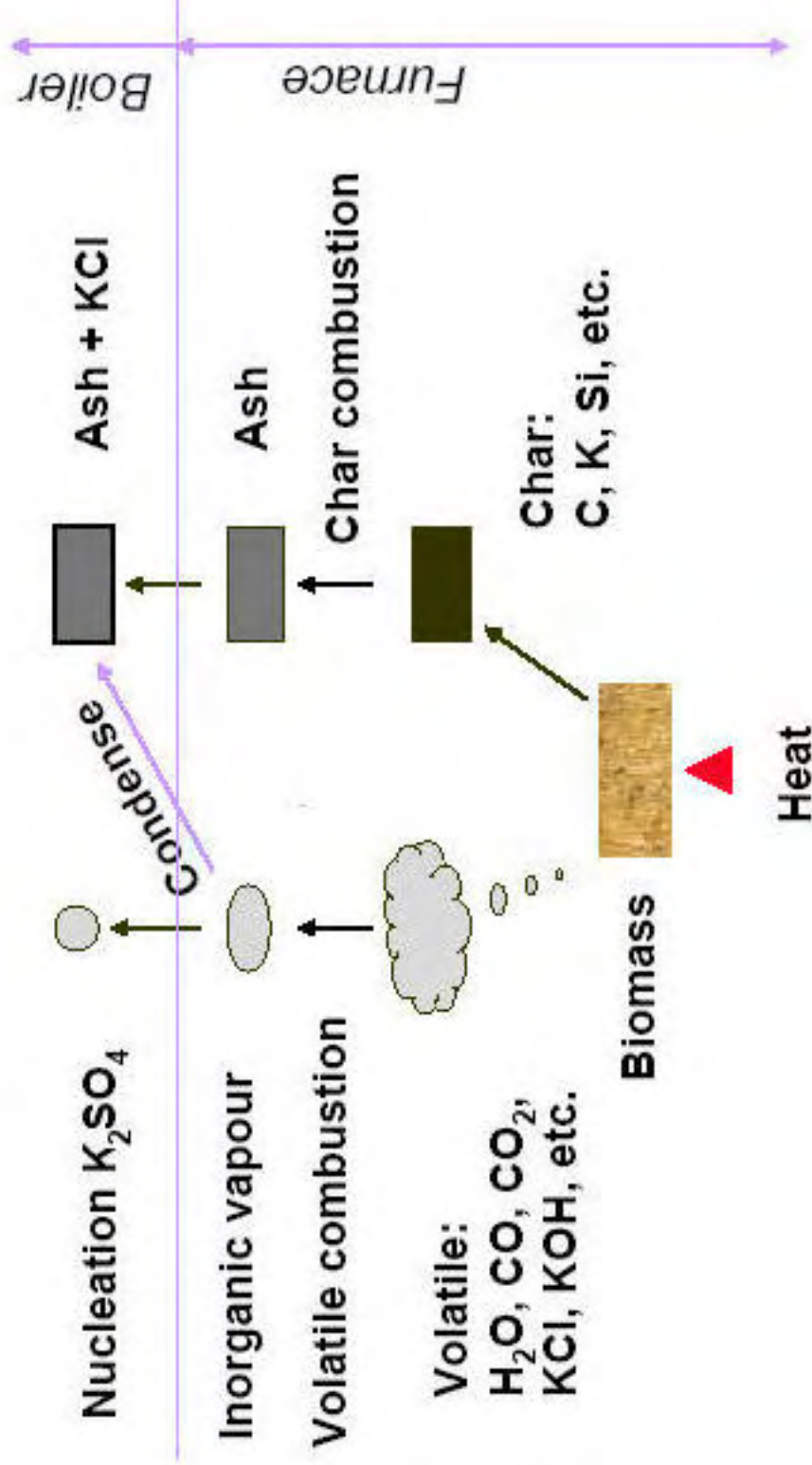
- Reduction in emissions, e.g.  $\text{CO}_2$ ,  $\text{SO}_x$ ,  $\text{NO}_x$

### Problems:

- High metal alkali content, e.g. K
- Deposition, slagging
- Low calorific value



# Formation of depositing particles



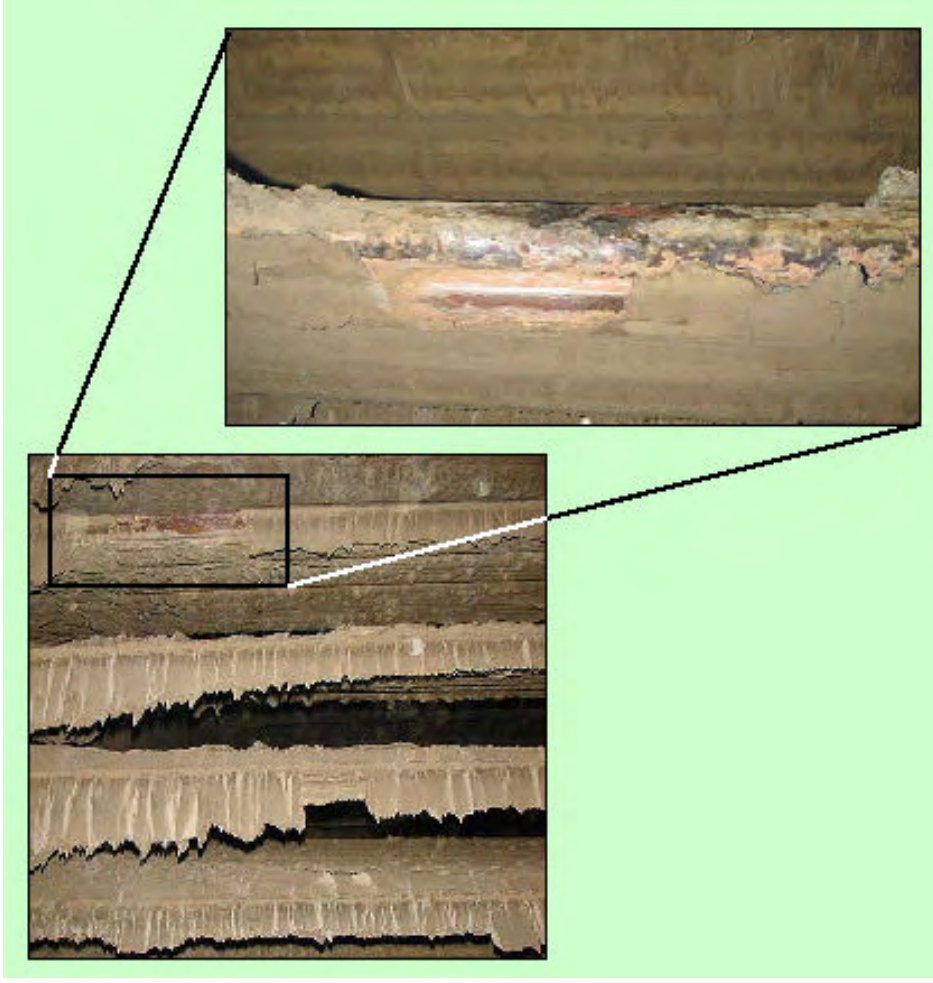
Release of K is significant  
at T in the range 700 – 1000 C

courtesy of Prof. A. Williams



# CHEMISTRY RELATED CHALLENGES

## - Fouling and corrosion



Problems in a large-scale  
fluidized bed combustor

Courtesy of Prof. M. Hupa

# CHEMISTRY RELATED CHALLENGES

## - Fuel impurities (1)

% by weight from ultimate analysis

	N	S	Cl	K + Na
Fuel oil	< 1.0	< 4.5	< 0.1	< 0.1
Coal	< 2.5	< 4.5	< 0.1	< 0.2
Wood	< 1.0	< 0.1	< 0.1	< 0.4
Straw	< 1.5	< 0.25	< 1.7	< 2.0
Other biomass	< 3.5	< 0.6	< 0.6	< 3.0

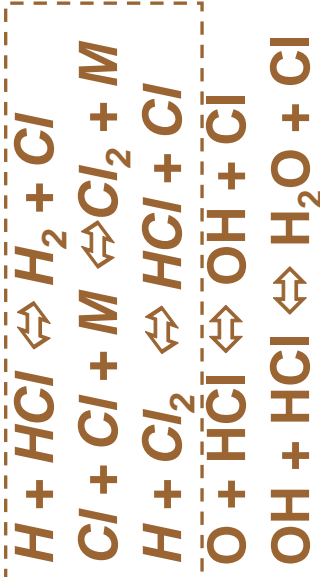
Plastic, paper and other waste should also be added

# CHEMISTRY RELATED CHALLENGES

## - Fuel impurities (2)

Effect of halogens in combustion:

Retardation through, e.g.,



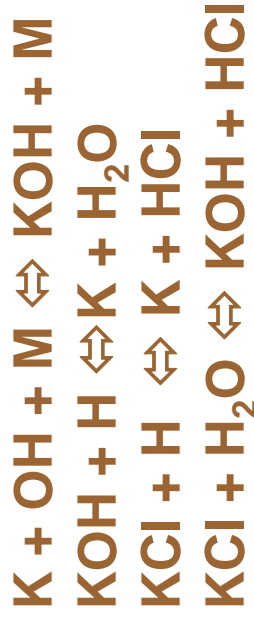
or competing promotion through



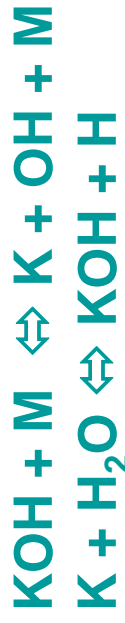
Note that there is a potential synergy between halogens and alkali metals present

Effect of alkali metals in combustion:

Retardation through, e.g.,



but, in the early stages when the radical pool is small, promotion can occur through the fuel-derived compounds which augments concentrations, e.g.,



Similarly, there can be N and S chemistry interactions ...

e.g., promotion of NO formation through



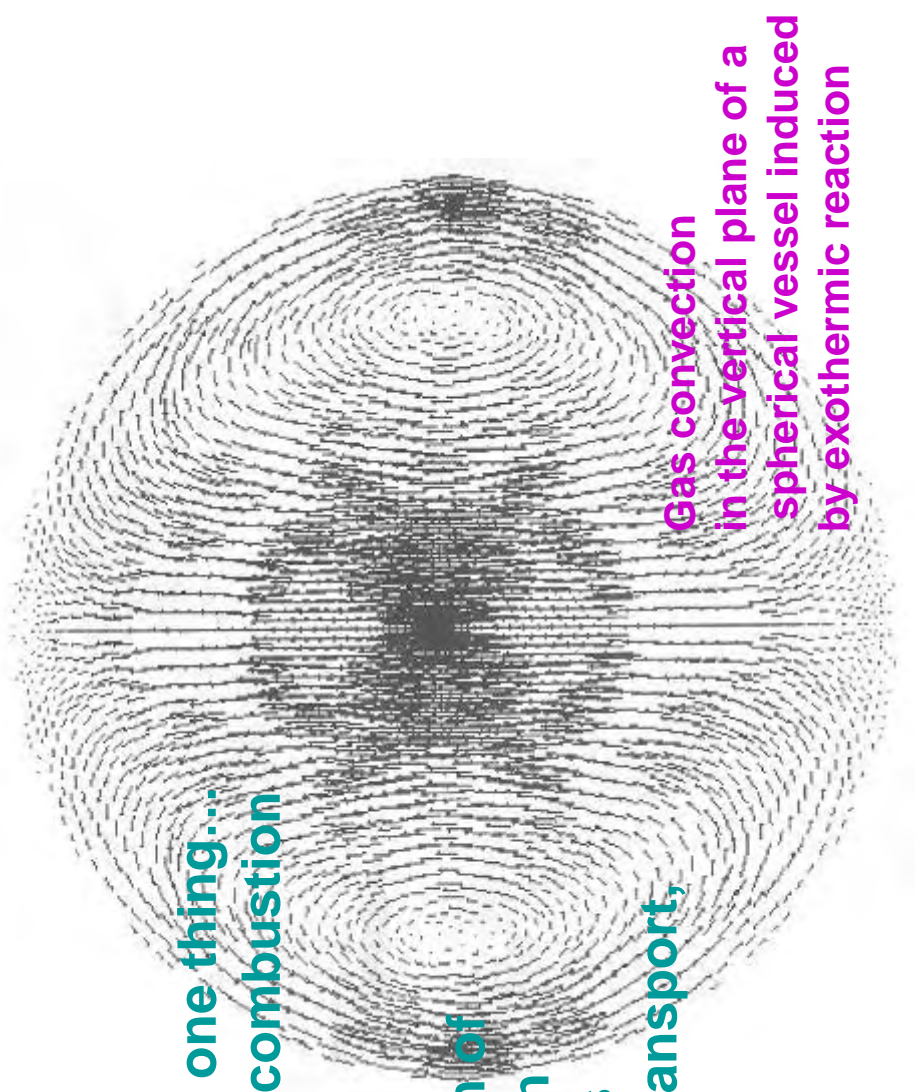
# CHEMISTRY RELATED CHALLENGES

## - Numerical simulation

The understanding and interpretation of the combustion kinetics involves numerical simulation, for which there are many proprietary programs. Most kinetic models are based on a CHEMKIN format

However, kinetic modelling is one thing...  
simulation of performance in combustion applications is another.

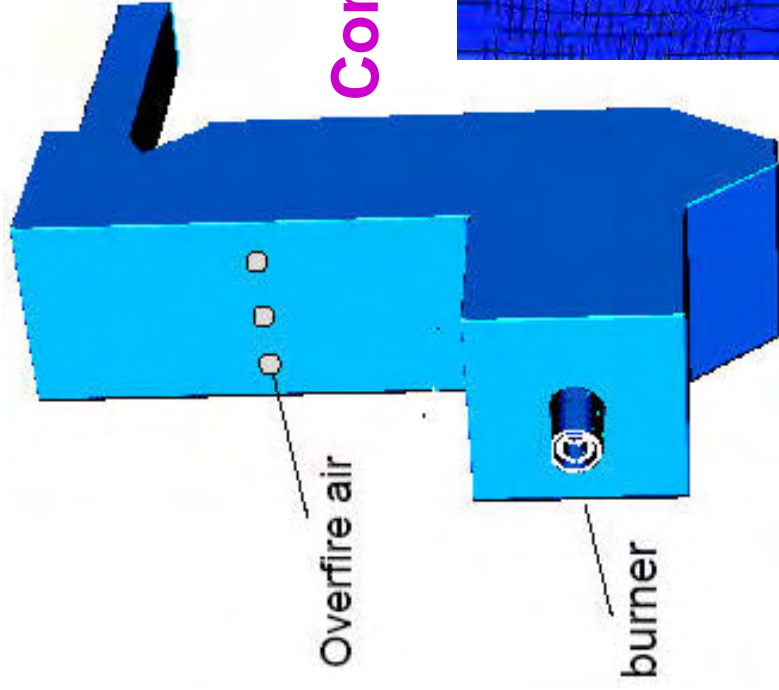
This requires the combination of  
“reduced kinetic” models with  
computational fluid dynamics  
to represent heat and mass transport,  
often including turbulence.



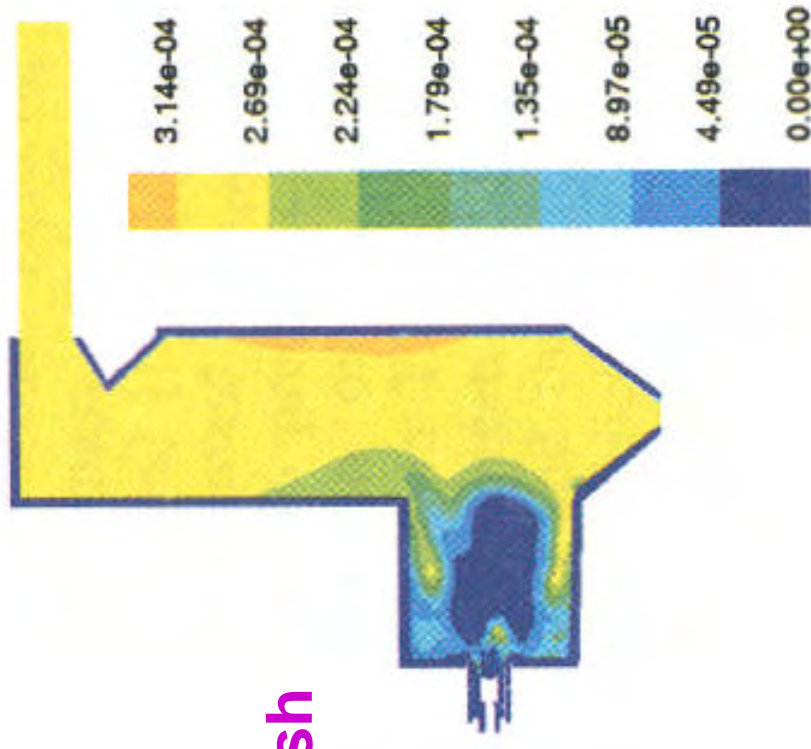


# Numerical simulation - example

Triple-staged, low-NO<sub>x</sub>, single burner furnace  
for co-firing coal and biomass

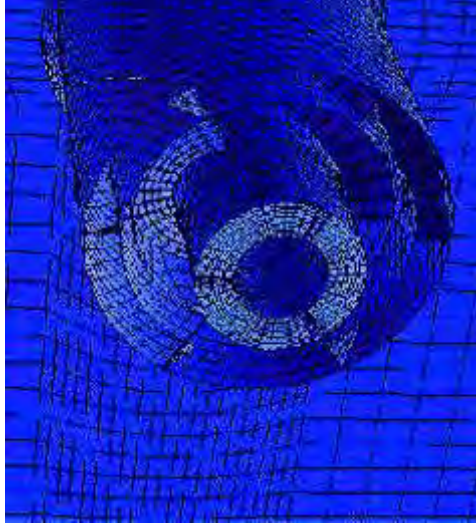


Overview



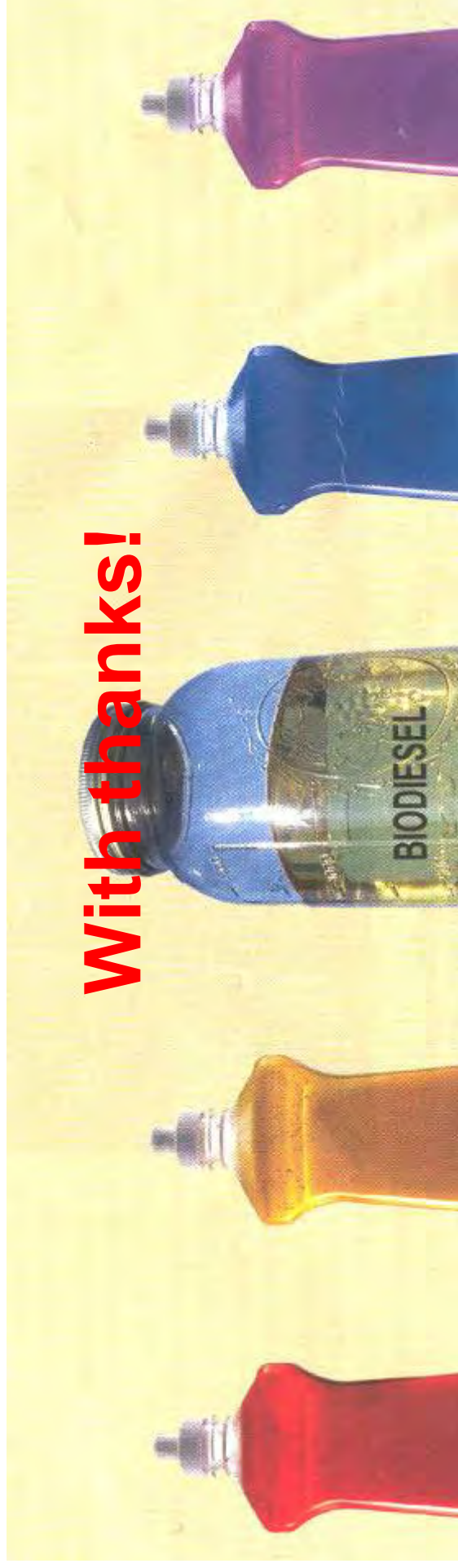
Predicted NO<sub>x</sub>  
mole fraction

Computational mesh



courtesy of Prof. Alan Williams

**“Mild green ionic liquids”**



**“Biodiesel production could become more environmentally friendly thanks to researchers in the UK who are using non-toxic ionic liquids to remove unwanted by-products...”**

“Chemistry World”, June 2007, by permission



UNIVERSITY OF LEEDS

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# **Cofiring of Coal and Biomass. A major Contribution to the Reduction of Carbon Dioxide**

J. M. Jones, L. Ma, M. Pourkashanian  
and A. Williams

*Energy and Resources Research Institute,  
Leeds University, UK*

# The Use of Co-firing

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- Widely used by power stations in the UK
- Most use about 10% biomass but can readily burn up to 25% thermal.
- A variety of fuels are used, mainly wood, olive and palm oil waste, cereal, straws and energy crops-SRC, miscanthus.
- Can generate more renewable energy than wind power in the UK,



# Fiddlers' Ferry Power Station

-uses 20% biomass (thermal)



# Advantages of Cofiring

---

- Co firing can be undertaken with existing power plants, and thus has high power generation efficiency. It is attractive in terms of the capital investment requirement and the generation cost.
- It can increase the amount of renewable energy/reduce CO<sub>2</sub> emission: -current level - 2%. EU target - 20% by 2020
- Almost any biomass material can be used-agricultural wastes, biofuel Therefore it is attractive in terms of security of supply
- Generally low in S and N

# Disadvantages

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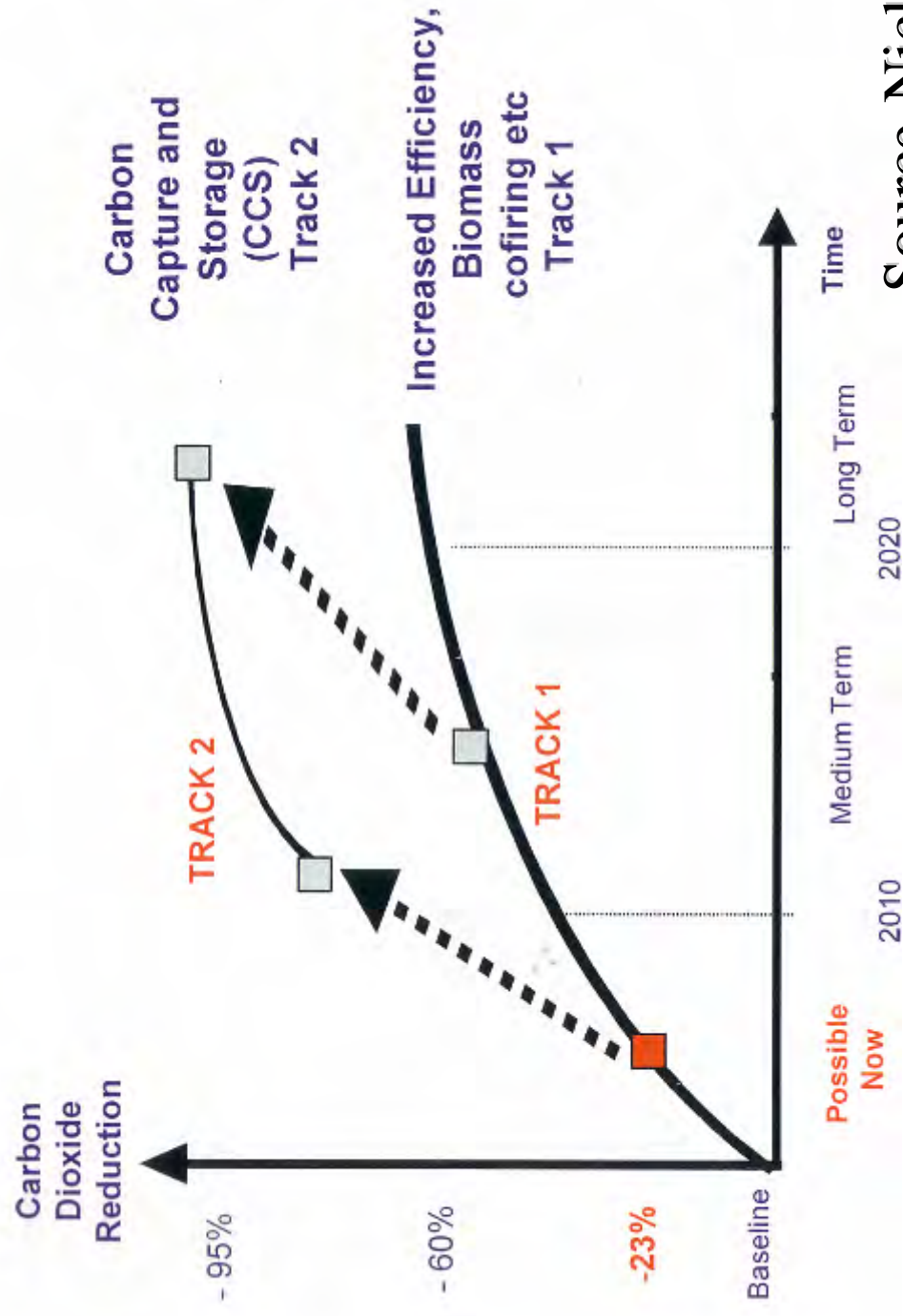
Biomass is a poor fuel- contains oxygen and a substantial amount of moisture

Contains potassium-can cause corrosion, produce fine particulates (KCl and smoke) and K, an important plant nutrient, is 'lost' with the coal ash

Biomass can be expensive-dependent on subsidies at present

May not be sustainable

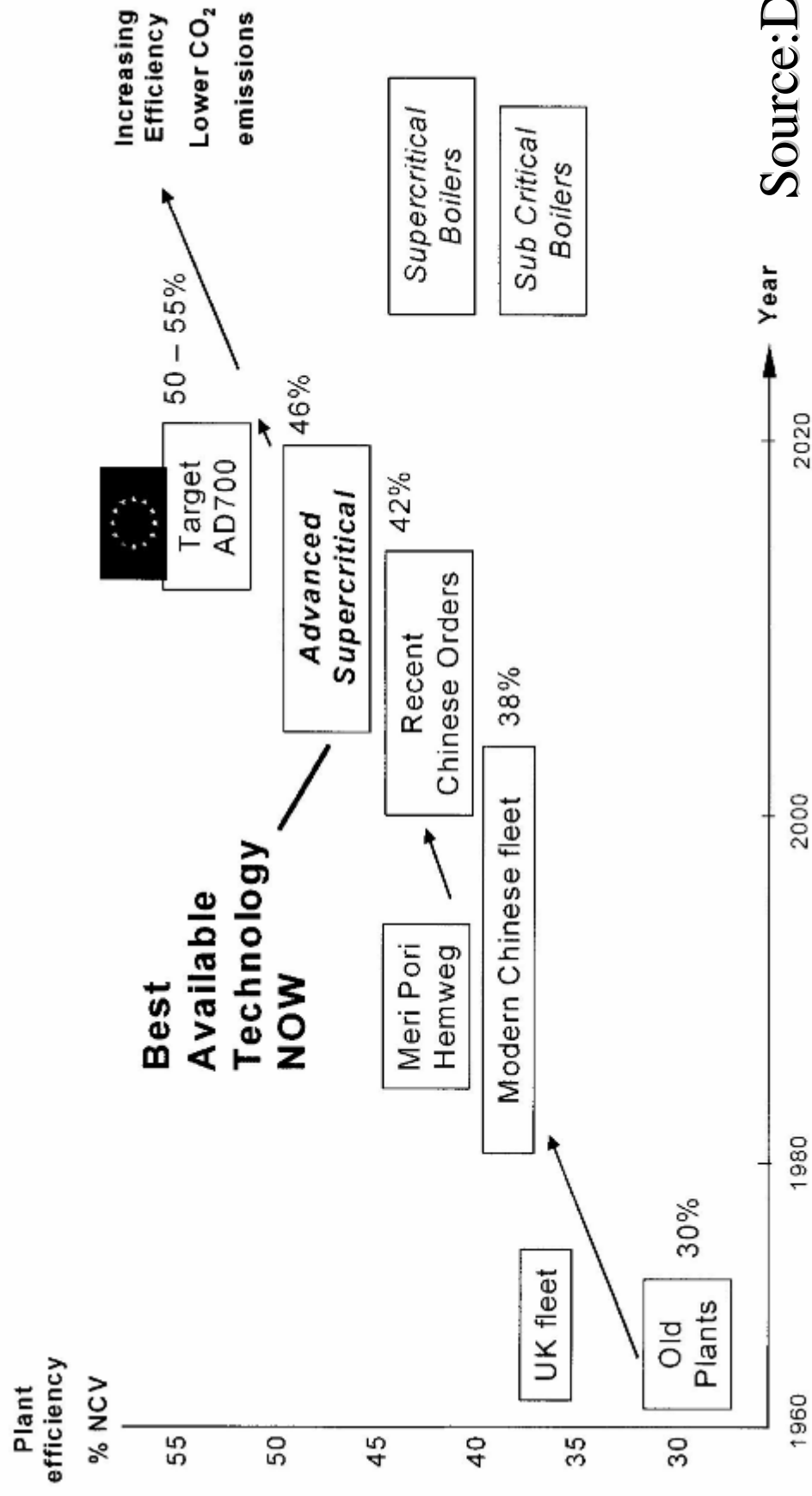
# CO<sub>2</sub> Abatement : Twin Track Approach



Source-Nick Otter



# Demand for High Efficiency, Clean, Coal-fired Power Generation Plants, with Biomass Co-firing and for CCS



# Fuel Handling Issues

---

Biomass can be milled with coal, or it can be milled in advance and added to the coal, or burned in a separate burner,

There can be problems with grinding and drying certain fuels, particularly fibrous materials such as wood.

These can be overcome by using large scale drying techniques or by torrefaction.

Other hazards are from dust and from spontaneous ignition.

# Biomass Handling





# Measurement of water content

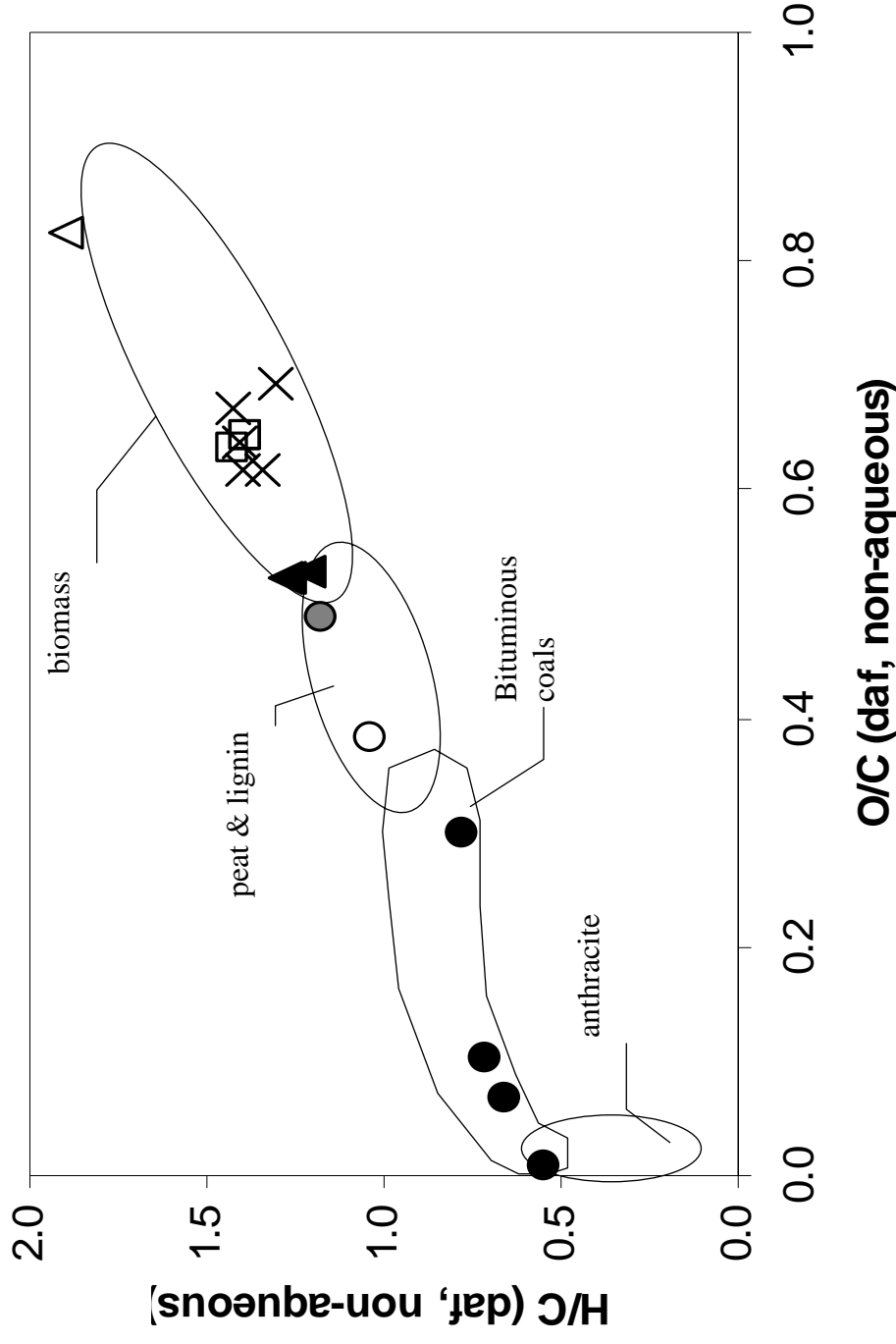




# Properties of Biomass Samples

Material	wt%		HHV kJg <sup>-1</sup>	moisture corrected (d.a.f)				
	moist.	Ash		C	H	O	V.M	F.C
Forage Maize (green)	4.47	11.72	16.1	47.77	6.15	40.80	95.99	4.43
Oat Straw	3.94	9.35	17.85	49.30	6.02	40.60	90.87	10.09
Barley Straw	3.94	11.30	18.5	50.45	6.39	41.50	89.47	10.34
Linseed Straw	3.16	7.93	17.65	48.87	6.20	43.70	94.89	5.11
Switch Grass	3.37	6.87	18.08	50.09	6.20	43.41	90	10
Reed Canary Grass	2.4	10.93	18.4	52.36	6.51	45.65	93.72	6.17
Miscanthus	1.92	10.93	19.08	53.15	6.40	45.99	95.94	4.1
Pine (Yorkshire)	4.97	2.56	18.62	52.63	6.10	39.84	83.8	15.98
Pine Wood Chip	3.02	5.27	18.8	54.00	6.07	40.98	85	13.76
Willow Coppice	5.37	5.86	17.69	52.69	5.92	41.82	87.58	12.1
Spruce	2.9	3.73	18.02	51.07	6.03	43.92	92.78	7.21
Oak	5.81	1.80	18.3	50.59	5.65	42.85	86.26	13.73

# Van Krevelen Diagram for Biomass Types



The van Krevelen diagram for biomass and coal: coalfication series, × straws, □ grasses, ▲ woods, ● peat, ● coal, ○ lignin, △ cellulose;



## Typical wood properties

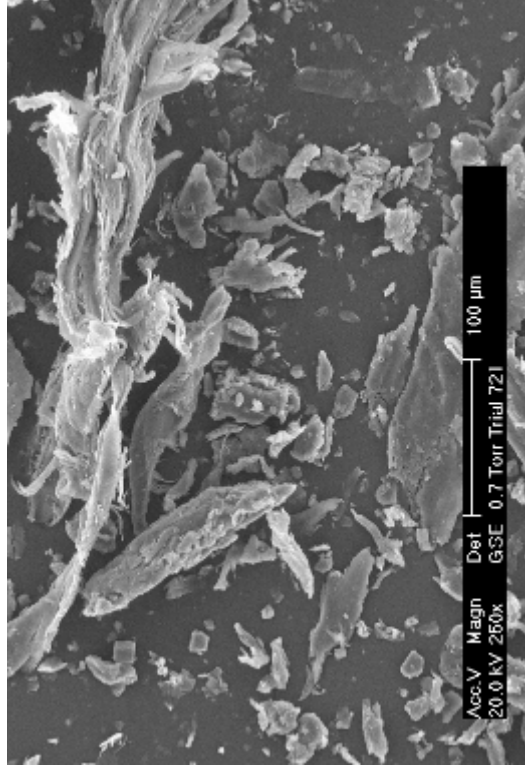
- Irregular shape
- High volatile, low ash
- High K, Cl content can be low or high
- Low calorific value



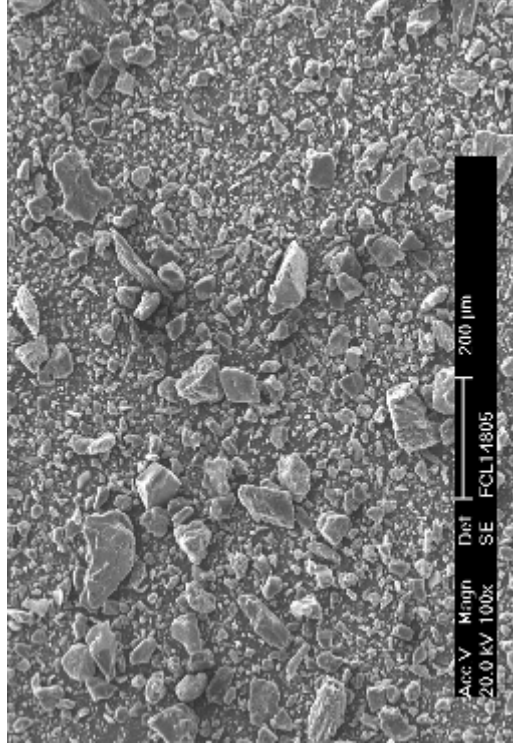
## As Received (%)

	Moist.	Volatile Matter	Fixed Carbon	Ash	K	Cl	N	CV (kJ/kg)
Wood	5.7	72.6	18.9	2.8	0.13	0.041	0.022	18750
Coal	2.8	30	51.4	15.8	-	0.01	1.87	26455

## Milled Wood

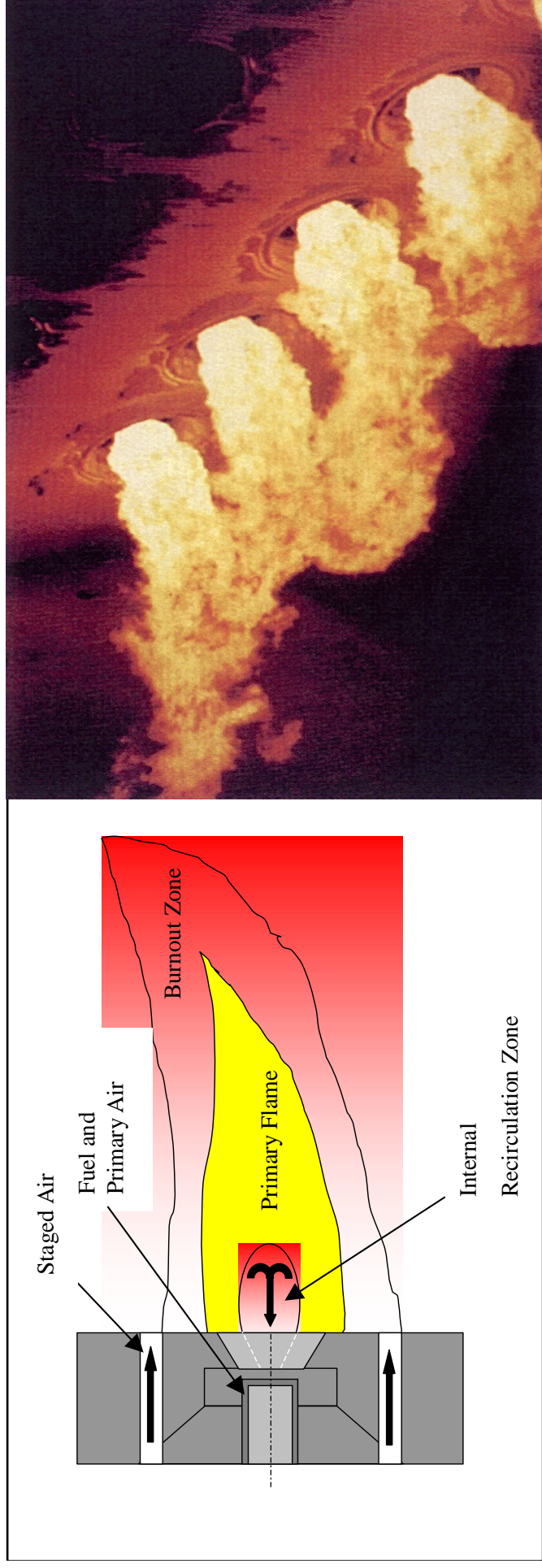


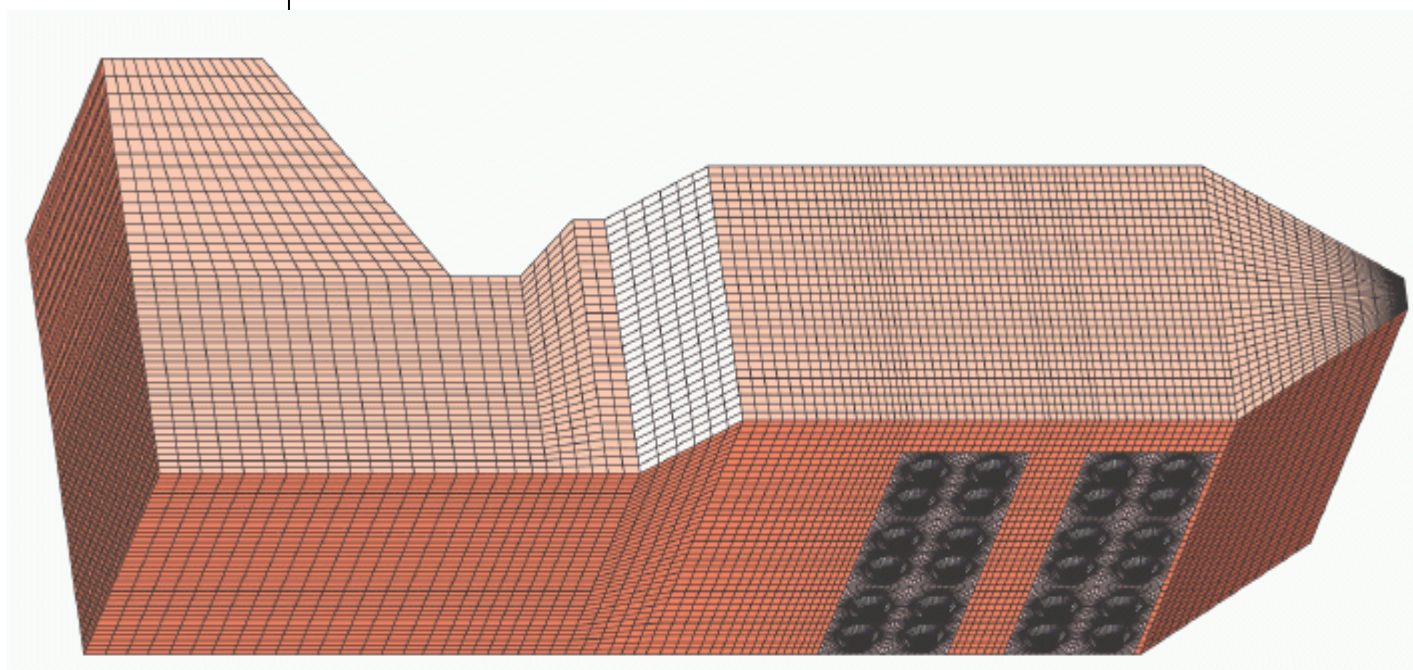
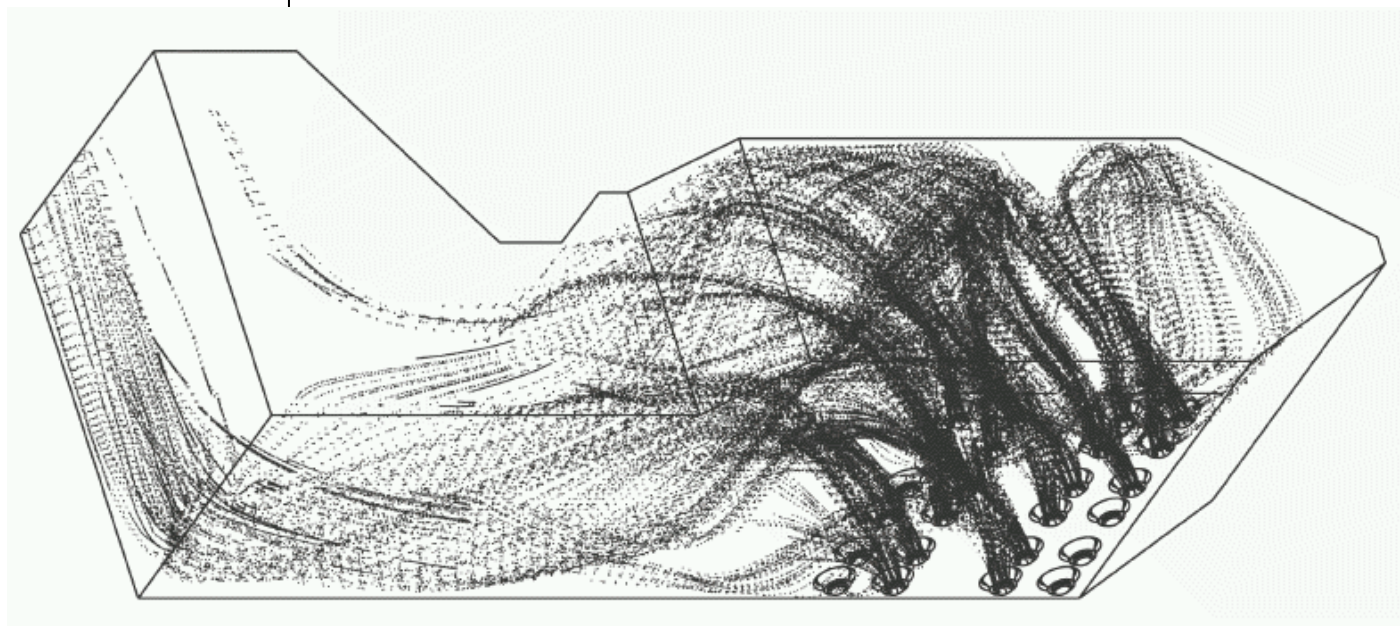
## PKE





# Power Station Furnace





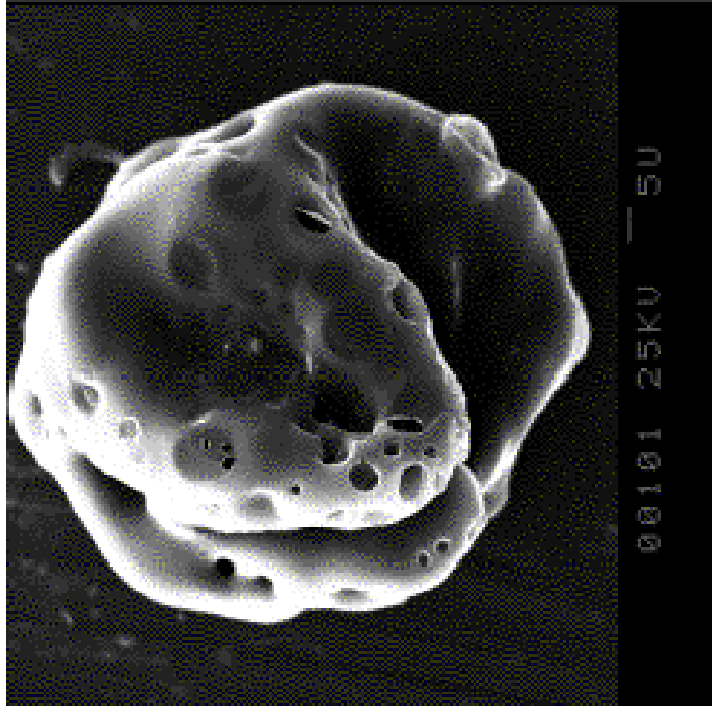
# The Combustion of Pulverised Coal and Biomass

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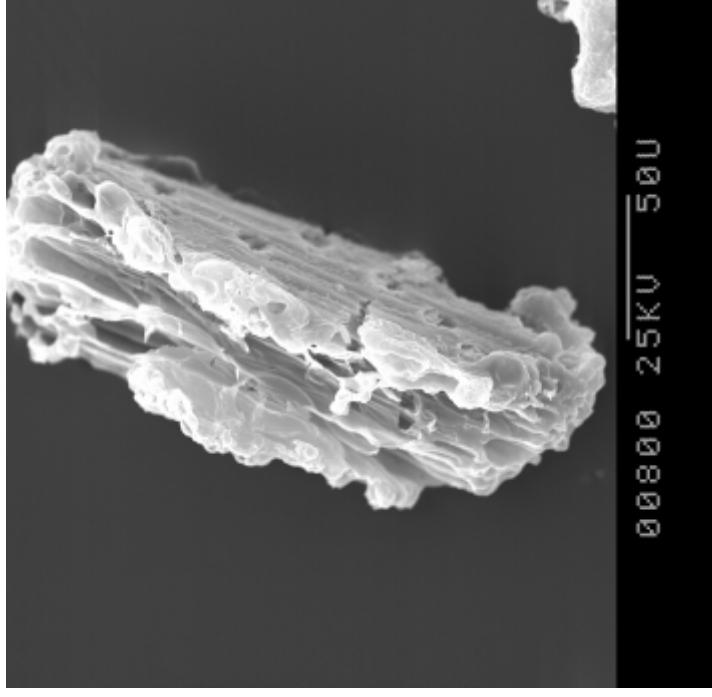
- The combustion steps are well established:
  - Heating and drying
  - Devolatilisation
  - Volatiles Combustion
  - Char Combustion
  - Sub-models relating to NO<sub>x</sub>, ash and metals

# Biomass Combustion: Particle Shape

Coal



Wood



:



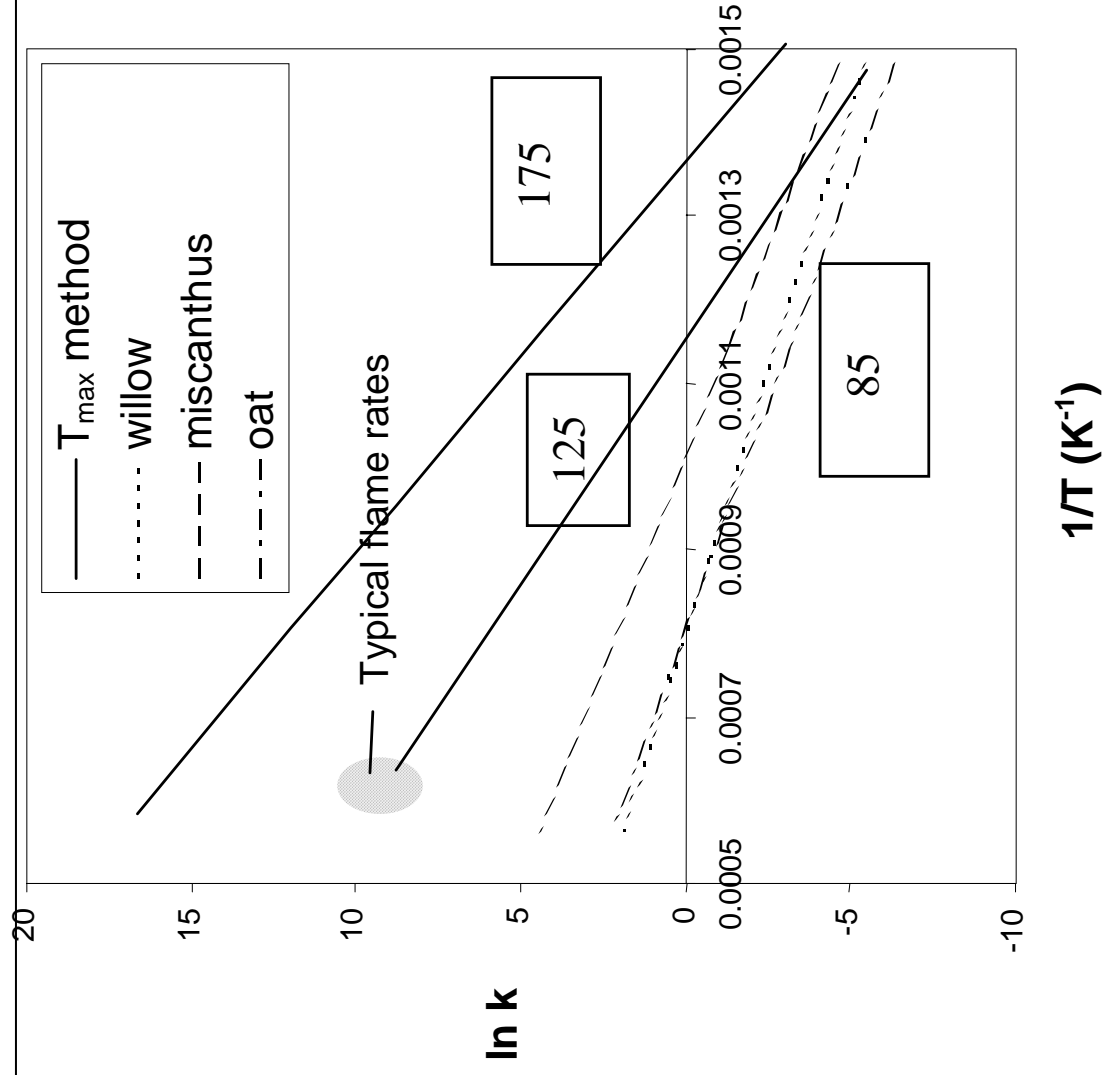
The rate of devolatilisation-both coal and biomass-is still a matter of some contention and a number of approaches have been used to model it. The simplest employ global kinetics, where Arrhenius expressions are used to correlate rates of weight loss with temperature. These simple models can be divided in two groups: single and multiple step reaction models. The first one has only one set of parameters and is widely used:

biomass= volatiles + char + tar

where

$$k_1 = A_1 \exp(-E_1/RT).$$

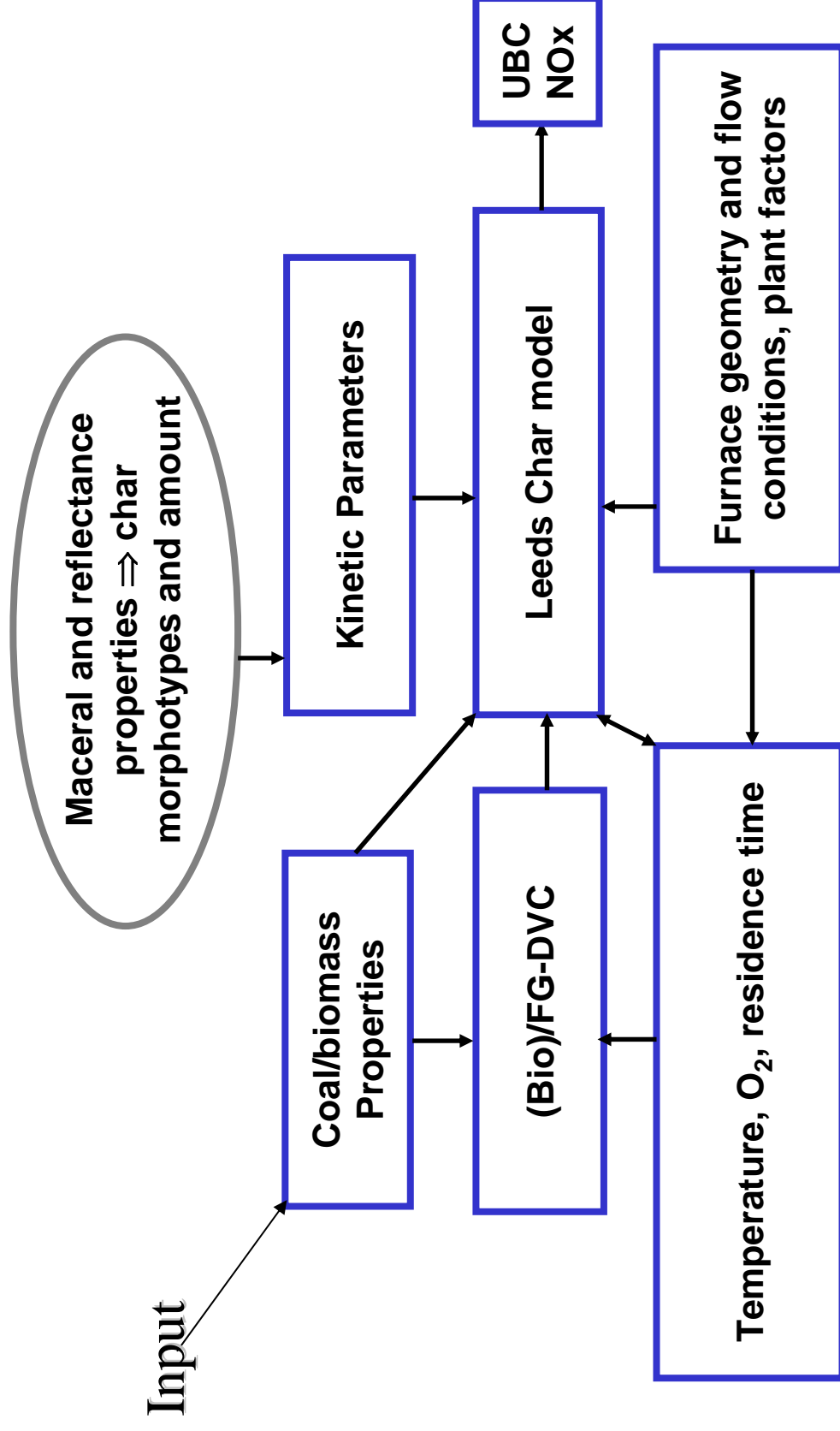
# Rate Data for Biomass Pyrolysis Kinetics Measured by Different Methods



# Biomass Char Oxidation

- Little information at high temperatures,
- Irregular shaped char particles are a problem
- Catalytic effects are small at high T,
- Rate of oxidation of O-containing char different to that of coal char,
- But only small amount of char produced

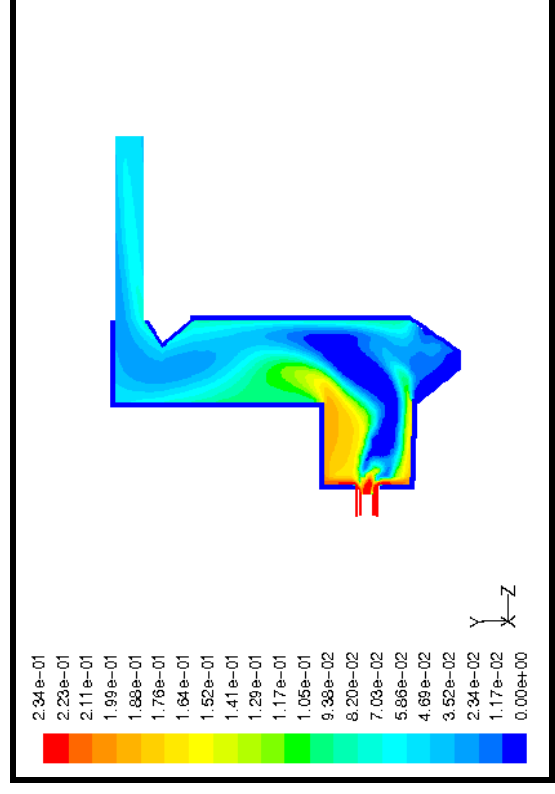
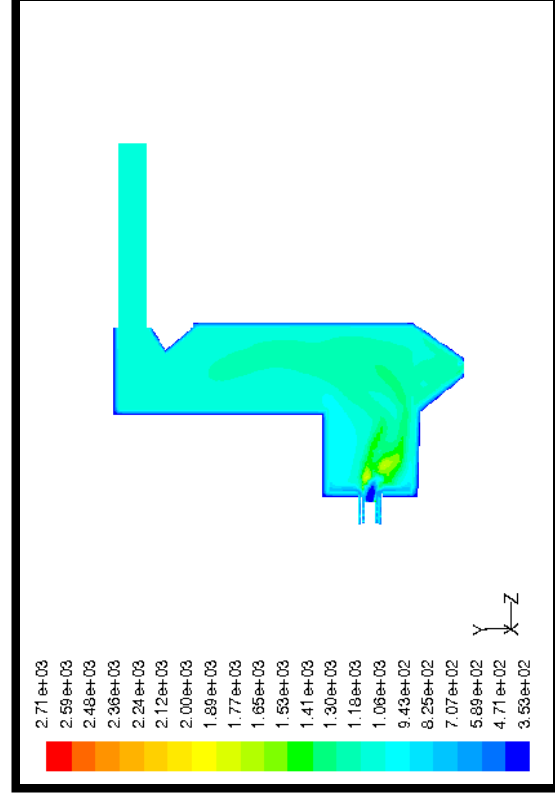
# LEEDS coal/biomass BURNOUT MODEL





# CFD Modelling of Coal/Biomass can be undertaken

Typical examples of computed T and O<sub>2</sub>



Contours of Static Temperature (K)

Contours of O<sub>2</sub> Mass Fraction

# Conclusions

---

**Large scale biomass co-firing is one of the most efficient and cost-effective approaches to generating electricity from renewable sources. Cofiring can make a significant contribution to the reduction of CO<sub>2</sub>**

**Biomass pre-mixing and co-milling is being practised successfully by a number of power station operators in Britain, continental Europe and the USA**

**A number of operators have plans to increase the biomass co-firing capabilities for long term operation. Biomass can be fired with coal up to 20% thermal or more.**

**There are however issues in relation to supply, and legislation.**

# Acknowledgements

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- Funding from EPSRC (Supergen) and BCURA is gratefully acknowledged
- Thanks to Bill Livingston (Doosan Babcock), Ben Goh (e.on Power Technology), Dave Waldron (Alstom) and Peter Stephenson (RWE npower) for useful information.



V I G N A N

# BIO – DIESEL FROM VEGETABLE OIL REFINERY WASTE

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&

\*\*A. V. Ajay Kumar

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Vignana's Engineering college::Vadlamudi

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\*\* Department of Petroleum and Environmental  
Engineering

University of Nottingham - NOTTINGHAM, UK





## ABSTRACT

- ❖ Bio diesel is an oxygenated, Sulfur free biodegradable, renewable, environmental friendly substitute for petroleum diesel fuel.
- ❖ Bio diesel can also added to petroleum diesel to create a bio diesel blend with favorable performance.
- ❖ This paper deals with the concepts related to the preparation of bio diesel from Soap Stock obtained from the Vegetable oils (Sun flower, Ground nut and sesame oil) refinery.



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# ABSTRACT

- ❖ Two step transesterification Process is used for preparation
- ❖ The effect of molar ratio of alcohol to soap stock
- ❖ The effect of reaction temperature, reaction time



## ABSTRACT

- ❖ The effect of free fatty acids & water present in the soap stock are studied and conditions are optimized
- ❖ The physical properties are estimated

This work enhances the availability of bio – diesel and decreases its cost



V I G N A N

# INTRODUCTION

The concept of bio – fuel dates back to 1885 when Dr. Rudolf Diesel built the first diesel engine with the full intention of running it on vegetative source. In 1912 he observed the use of vegetable oils for engine fuels may seem insignificant today. But such oils may in the course of time become as important as petroleum and the coal tar products of present time. In 1970 scientists discovered that the viscosity of vegetable oils could be reduced by a simple chemical process and that it could perform as diesel fuel in modern engine.





# INTRODUCTION

- Since then the technical developments have come a long way and the plant oil today has been highly established as bio – fuel.
- Bio diesel is a renewable liquid fuel that can be produced locally thus helping reduce the country's dependence on imported crude.



V I G N A N

# INTRODUCTION

- India is one of the largest petroleum consuming and importing countries.
- India imports about 70% of its petroleum demands.
- The current yearly consumption of diesel oil in India is approximately 40 million tones consuming about 40% of the total Petro – Product Consumption.(1)



## INTRODUCTION

- It is known that Bio diesel is non –toxic & environmental friendly
- It produces substantially less carbon monoxide and 100% less sulfur dioxide emissions with no unburnt hydro carbon.
- Bio diesel can be used alone or mixed in any ratio with conventional diesel.
- The preferred ratio of mixture ranges between 5 and 20%



# INTRODUCTION

- It has good potential for rural employment generation (2).
- Semi refined and refined vegetable oil are the predominant feedstocks for the production of bio – In India these vegetable oils are a rich part of diet. Hence relatively high costs render the resulting bio – diesel unable to compete with petroleum derived fuel.
- Soap Stock (SS), a by – product of the vegetable oil industry which contains up to 70% fatty acids is investigated to produce bio – diesel
- SS can be considered as a potential source as it contains large amounts of free fatty acids (45-50%)

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## INTRODUCTION

- This could increase availability of bio – diesel while decreasing its cost.
- Soap Stock (SS) consists of a heavy alkaline aqueous emulsion of liquids, containing about 50% water, with balance made up of free fatty acids (FFA), phosphoryl glycerol, triglycerols etc.,
- Soap Stock (SS) is generated at a rate of 5% of the volume of crude oil refined, which equates to an Indian production of approximately 1 million metric tones.



# INTRODUCTION

- Primary challenge in the use of Soap Stock (SS) as a feedstock for bio – diesel production is the same as that faced by waste cooking oil conversion into bio – diesel (4-6).
- It was reported that oils containing high percentage free fatty acids can not be effectively converted into bio-diesel using only alkaline catalysts(4,7)



# EXPERIMENTATION

## Materials:-

- Soap stock Samples: Three different Soap Stock samples were utilized in this study. They were derived from ground nut oil, Sunflower oil and Sesman oil (Vijaya Agro Products – VJA).
- All other chemicals are obtained from Qualigens India limited. They are of high pure and used as they are.



# EXPERIMENTATION

## Methods:-

Three different approaches are adopted to produce bio – diesel from Soap Stock (SS).

1. The Soap Stock (SS) is first converted to a glycerol mixture by reaction with glycerol and then transesterified into a mixture of methyl esters.(6)



V I G N A N

## EXPERIMENTATION

2. In this method dry Soap Stock (SS) was pulverized to a fine powder and the esterification is carried in presence of Sulfuric acid and methanol.(6)
3. Ferric Sulfate Catalyzed methanolysis:-  
Conversion of SS to bio – diesel using solid ferric sulfate catalyst. This is a two step process in the first step the mixture of Soap Solution, Methanol and Ferric sulfate is heated at 90°C.





## EXPERIMENTATION

- The mixture is then cooled and centrifuged to separate Ferric Sulfate.
- In the second step Potassium Hydroxide is added to catalyze the transesterification reaction.
- The reaction is carried at 65°C, and then excess of methanol is recovered under vacuum at 50°C.



# EXPERIMENTATION

- The mixture is left to settle to separate into two layers. The upper oil layer is the bio – diesel and un reacted triglycerides and the lower layer is water with insoluble catalyst that is recovered for further use.
- The time schedules followed are 1, 2 and 3 hours the weight percentage of catalyst taken is 1,2 and 3.



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# EXPERIMENTATION

The percentage conversion of SS into the Bio – diesel is calculated from the Acid Value of the layer. The following equation is used.

Percentage Conversion =

$$\left( 1 - \frac{AV_{oil}}{AV_{ss}} \right) \times 100$$

Where  $AV_{oil}$  = Acid Value of oil  
 $AV_{ss}$  = Acid Value of Soap Stock.



# EXPERIMENTATION

## Analysis of Bio – diesel:-

- With the help of Gas Chromatography equipped with Flame Ionized Detector dried crude bio – diesel samples are analyzed.
- Nitrogen gas is used as carrier gas. The lauric acid methyl ester is used as reference material.



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# EXPERIMENTATION

- The analysis is performed by dissolving 0.5g of bio – diesel sample and 0.05gm of lauric acid methyl ester into 10ml of n-hexane and injecting 1 $\mu$ l of this solution in the Gas Chromatography.
- The purity of the crude Bio – diesel is calculated from the area of sample over the reference area.





# EXPERIMENTATION

- The following equation is used.

% purity =

$$\frac{\text{Area of Bio} - \text{diesel} / \text{area of reference} \times \text{weight of reference}}{\text{Weight of dried bio} - \text{diesel}} \times 100$$

- The samples are withdrawn from reacting mixture at different time intervals and analyzed to know the effect of time on percentage conversion.

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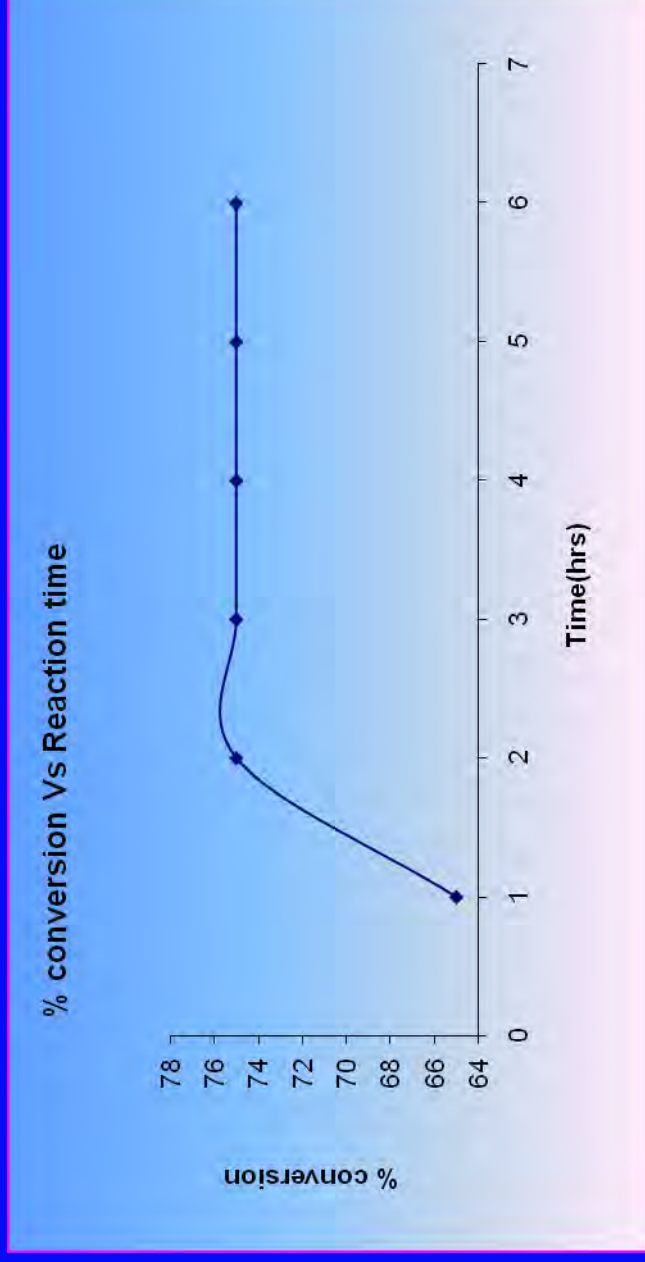
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# RESULTS AND DISCUSSION

**1. Effect of Time:-** The effect of reaction time on the percentage conversion is shown in the Fig (1). From the figure it is clear that within an hour the 75% of the free fatty acids were found to be converted in bio-diesel. It also found that almost 95% conversion after 2 hours and no remarkable conversions were noticed even up to 5 hours of time.





# RESULTS AND DISCUSSION

## 2. Effect of Weight Percentage of Catalyst:-

The effect of weight percentage of Ferric Sulfate catalyst on percentage conversion is shown in the Fig (2). The conversion was found to be very slow when no catalyst is used, however upon the addition of 1 wt% of ferric sulfate the percentage raised to 60% . The further increase in amounts 2 wt% and 3 wt% the conversions were found to increase to 90 and 95 respectively.

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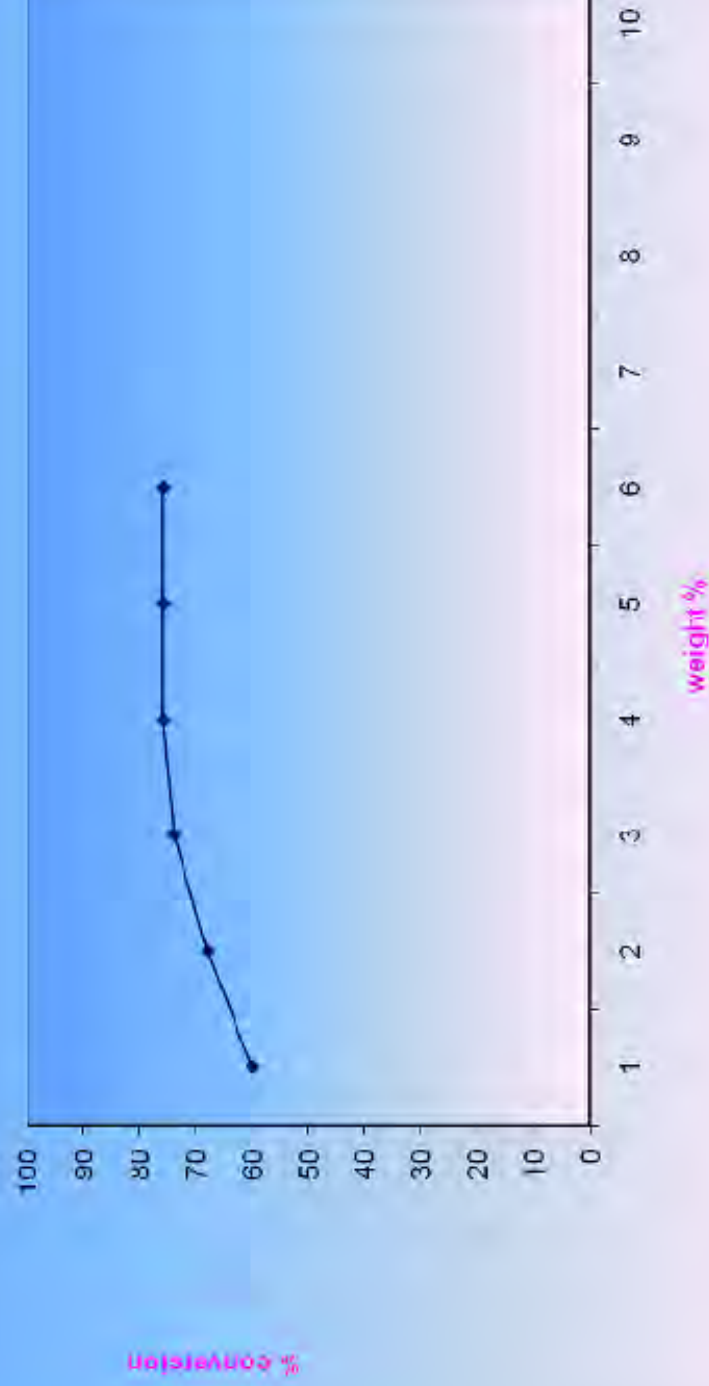
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## RESULTS AND DISCUSSION

Effect of Catalyst weight on % conversion





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## CONCLUSIONS

The process is a heterogeneous two step catalytic, where ferric sulfate catalyzed methanolysis. The catalyst is found to be very effective and easy to handle. It can be reused. The optimum condition are 2 hours time 2 wt% catalyst. If the process is further explored the most of available Soap Stocks can be converted into very useful Bio-Diesel.





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