2nd Generation Ethanol -A Prospective-



By Dr S.K.PURI Indian Oil Corporation Limited , R&D Centre , FARIDABAD 22nd Jan., 2016

BIO-FUELS



Fuel produced from renewable biomass material, commonly used as an alternative, cleaner fuel source.

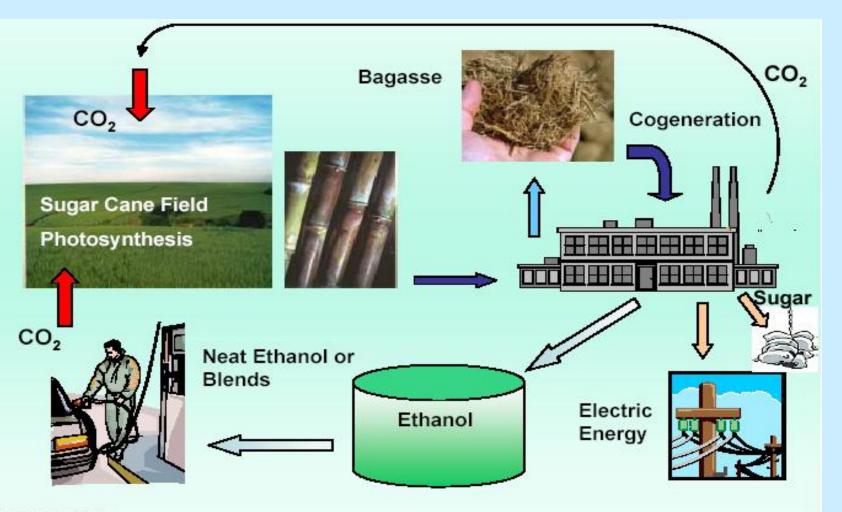
- Bio-diesel
- Bio-ethanol
- Bio-butanol
- Bio-Jet fuel
- Bio-oil /Pyrolysis oil
- Green Diesel
- Bio-methane

Why Bio-Fuels ?



- Renewable Nature
- Environment Friendly
- Energy Security
- Rural Development
- Compatible with Petroleum Diesel
- High Performance
- Energy Sustainability

CO2 Cycle of Ethanol production fro Sugarcane



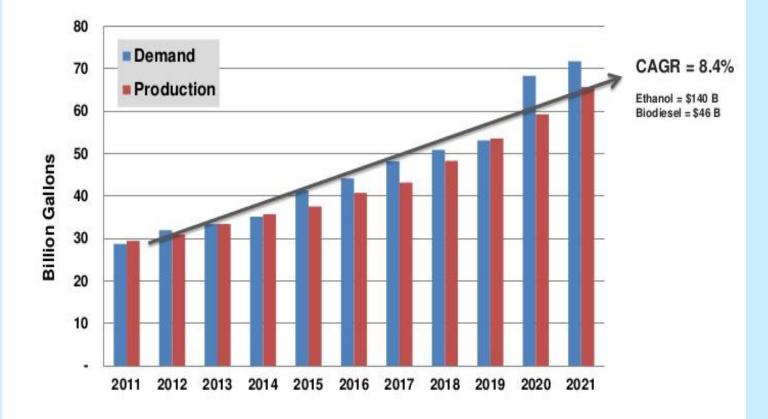
SOURCE: ADS

Global Forecasts by Fuel





Biofuels Demand & Production, World Markets: 2011-2021



Bio-ethanol as Transport Fuel



- Ethanol advantages as Transport Fuel;
 - Octane enhancer
 - No engine modification required for E10 and lower blends
 - Higher compression operation of the engine feasible
- Environmental benefits;
 - Lower emissions of CO, VOC and hydrocarbons
 - Lower CO2 emissions with high compression ratio
 - Complete CO2 cycle
 - Higher biodegradability and low toxicity

5% Ethanol blending in gasoline is being done in India. Further, BIS has issued specs for E10 blending.

Ethanol: India Status



- Up to 10 % ethanol blending with gasoline IndianOil The Power of Power
- Only source for ethanol is sugarcane molasses
- Ethanol is in short supply
- Alternate sources like cellulosic ethanol are necessary
- Enzymes are required for critical step of saccharification
- Specific cellulase cocktails for each feedstock and pre-treatment methods

CURRENT STATUS



- Mo P&NG finalized fixed delivered price of Ethanioi ^{IndianOil} ^{Ite Power of Po}
- Committee constituted on Bio-fuels implementation program
- Ethanol in gasoline in 2014-15: 2.3% (67Cr Lts)
- EOI issued for 266 Cr Lt ethanol
- Quantity finalized : 120 Cr Lt
- Short fall : 55%
- Ethanol presently is from sugarcane molasses

2nd Generation Ethanol Technology with alternate feedstocks necessary

Opportunities, Trends and Outlook



- Demands for ethanol fuel are growing rapidly.
- The U.S. recently revised its national biofuels targets from 7 billion gallons to 17 billion gallons by 2017, or approximately a 20% replacement of transportation fuels in the next ten years.
- Europe, Brazil, China and India each aim to replace 5% to 20% of onroad gasoline consumption with ethanol.
- India consumes about 20 MMTPA of gasoline
- In India , considering 10% blends, the requirement of ethanol would be 2 MMTPA, which is a big challenge to meet
- In India ethanol is being produced from molasses and Govt. does not permit to produce ethanol from corn or other food grains
- Therefore, these global demands are driving new investment into lignocellulosic ethanol R&D.

India's Biomass Production



Dry Biomass	Gross	
	(million tons/ year)	
Agriculture	583.7	
Weeds	80.0	
Forest	764.4	
Wastelands	237.3	
Total	1665.4	

The estimated total biomass energy potential is nearly double the fossil energy consumption

Biomass Sources





Sugar Cane



Corn Starch



Corn Fiber



Paper

Wood Chips

Stover



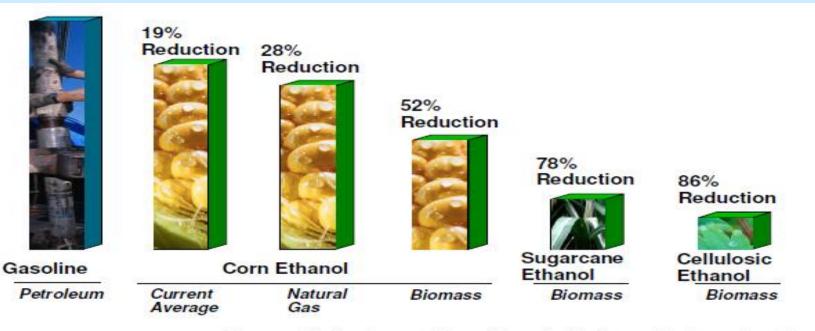
Switch Grass

Cottonwoods

Why Cellulosic ethanol?



- 1.Cellulosic ethanol is widely recognized as one of the promising way to meet the need of clean transport fuel to part replace gasoline
- Environment friendly, has a potential to reduces green house gas emission by ~90%.
- 3. No food Vs fuel conflict



*Faraco & Hadar, Renewable and Sustainable Energy Reviews. (2011) , 15, 252-266

Ethanol Feed Stocks & Production Technologies



- Sugar cane/ Beet molasses & juice ____
- Grain and Tubers (other starchy sources)
- Lignocellulosic Biomass



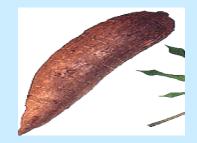
Fermentation

- Enzymatic saccharification /Acidic Hydrolysis
- Pretreatment sacchrification /acidic hydrolysis & enzymatic fermentation





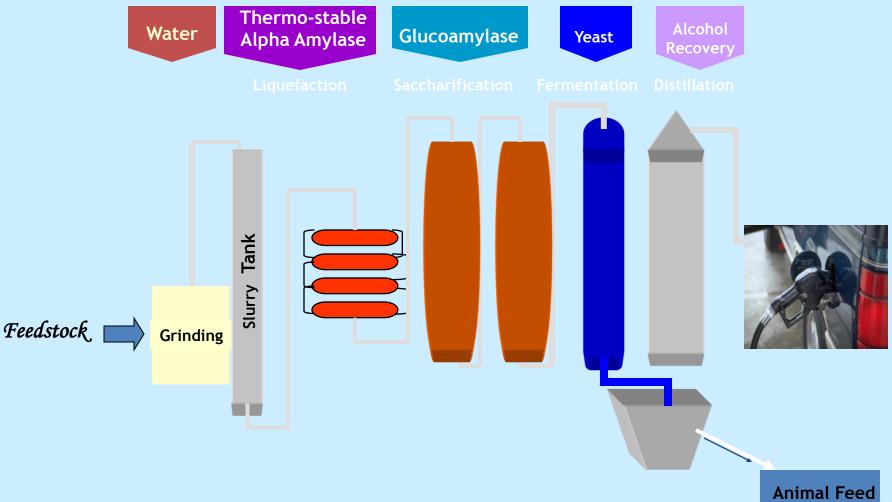




IndianOil The Power of Possibilities

Ethanol Production from Starchy Crops

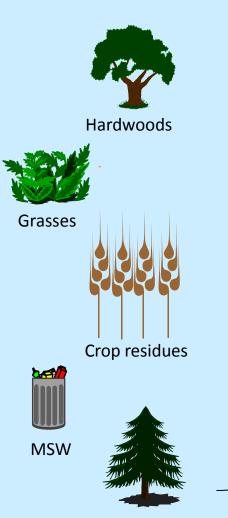




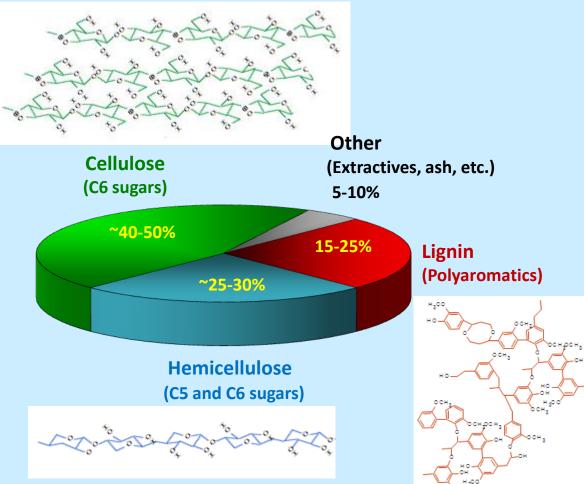
Source : SUSTAINABILITY AND THE BIOBASED ECONOMY, Genencor International, Inc.

What is Lignocellulosic Biomass?



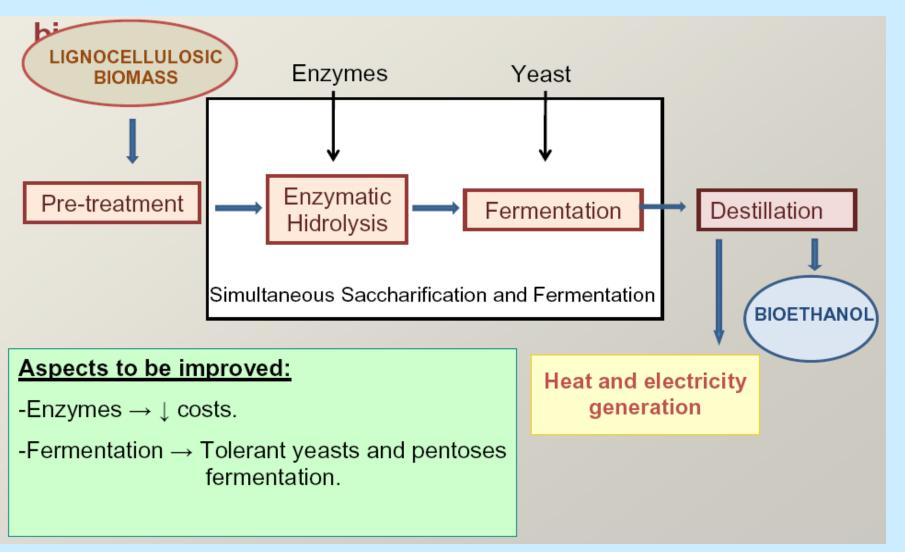


Softwoods



BIOETHANOL PRODUCTION FROM LIGNOCELLULOSIC BIOMASS





Lignocellulosic Biomass IndianOil The Power of Possibilities **TYPICAL PROCESS OUTLINE** Most Complex Step STEP 1 **Pre-Treatment Step** High in CAPEX Requires complex enzymes **Saccharification** STEP 2 High in OPEX Established for glucose New technology for pentose **Fermentation** STEP 3 Innovations regd for better performance STEP 4 Separation/Purification Alcohol

Steps involved



• Pretreatment of biomass

-Produces Lignin and cellulose with hemicellulose

- De-saccharification of polysaccharides
 - Enzymatic
 - -Chemical means
- Fermentation of monosacchrides
 - Enzymatic

METHODS OF PRETREATMENT





Mechanical fragmentation, Pyrolysis, Steam explosion, ammonia fibre explosion, CO_2 explosion, Ozone pretreatment, Milling & Irradiation



Oxidative delignification, Acid hydrolysis, (Concentrated Acid and Dilute Acid), Alkaline Hydrolysis, Solvent extraction



Enzyme hydrolysis, Pretreatment with bacteria, fungi & actinomycetes

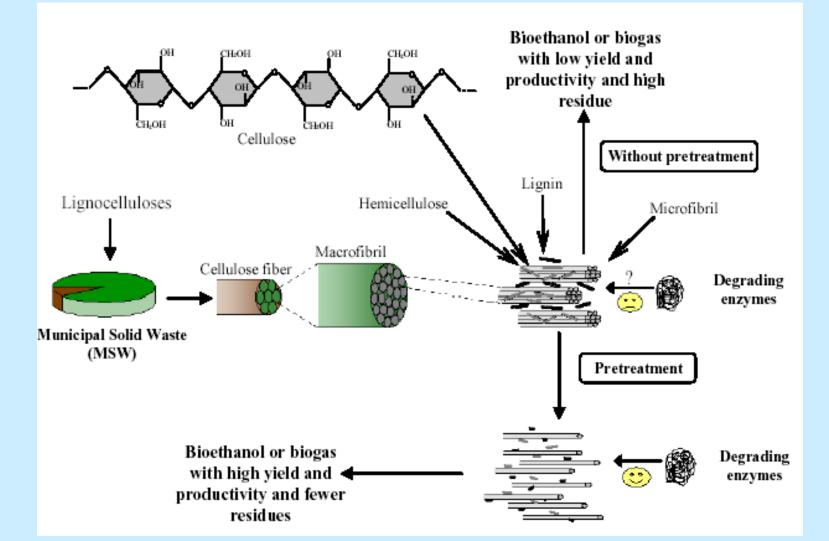
Why pretreatment?



- Enzymatic hydrolysis of lignocelluloses without pretreatment is usually not so effective because of high stability of the materials to enzymatic or bacterial attacks.
- Increase the accessible surface area
- Hydrolyse hemicellulose
- Decrease crystallanity which improve enzymatic hydrolysis

Effect of pretreatment on accessibility of degrading enzymes





Factors affecting pretreatment



- Crystallinity: Lower the better
- Accessible surface area: Higher the better
- Presence of lignin: Lower the better
- Presence of hemicellulose: Lower the better
- Degree of polymerization: Lower the better

Mechanical fragmentation



- Milling- cutting the lignocellulosics into smaller particles
- Reduction of particle size, crystallinity and degree of polymerization
- Increased available surface area
- No inhibitor production
- High energy requirement
- Unable to remove lignin and hemicellulose which restricts the access to enzyme

Could be very good in combination of other methods!

Steam explosion



- Steam (240°C) and pressure application followed by release of pressure and sudden cooling reduces formation of inhibitors
- Remove hemicellulose
- Better accessibility for enzyme hydrolysis
- Addition of H₂SO₄ or CO₂ can effectively improve the enzymatic hydrolysis, decrease the inhibitors and more hemicellulose removal
- Destruction of xylan, incomplete disruption of lignincarbohydrate matrix
- Harsh condition can lower the enzymatic digestion

This is one of the best suited and fulfils all the requirement

Ammonia fiber explosion



Exposure to liquid ammonia at high temp (90-100°C) and pressure
 Ammonia recycling is possible
 Do not produce inhibitors

- Ammonia depolymerizes lignin
- Removes little hemicellulose and decrystallizes cellulose

Alkali Treatment



- Solvation and saphonification causes swelling of biomass
- Lignin removal and cellulose swelling
- Separation of lignin-carbohydrate linkage
- Loss of fermentable sugar
- Production of inhibitors
- Long time and high base concentration required
- Disruption of lignin structure

Acid treatment



- Treatment of acidic water at high temperature and pressure
- Solubilization and swelling of hemicellulose
- Decrease in polymerization and crystallinity of cellulose
- Strong acids poses the risk of inhibitor production so, mild acids are better
- Condensation and precipitation of lignin is unwanted reaction
- Requires neutralization and corrosion an issue
- High investment and maintenance cost
- At low pH formation of inhibitors

Biological treatment



- Use of micro-organism to treat the liginicellulose
- White and soft rot attack both cellulose and lignin
- Brown rots mainly attack cellulose
- Cost effective and eco-friendly
- Extremely slow process

Commonly used pretreatment processes



Pretreatment process	Advantages	Disadvantages	
Steam explosion	Causes hemicelluloses degradation and lignin transformation; cost-effective	Destruction of a portion of the xylan fraction; generation of compounds inhibitory to microorganisms	
AFEX	Increases accessible surface area, removes lignin and hemicelluloses to an extent; does not produce inhibitors for downstream processes	Not efficient for biomass with high lignin content	
CO ₂ explosion	Increases accessible surface area; cost- effective; does not cause formation of inhibitory compounds	Does not modify lignin or hemicelluloses	
Ozonolysis	Reduces lignin content; does not produce toxic residues	Large amount of ozone required; expensive	
Acid hydrolysis	Hydrolyzes hemicelluloses to xylose and other sugar; alters lignin structure	High cost; equipment corrosion; formation of toxic substances	
Alkaline hydrolysis	Removes hemicelluloses and lignin; increases accessible surface area	Long residence times required; irrecoverable salts formed and incorporated into biomass	
Organosolv	Hydrolysis lignin and hemicelluloses	Solvents need to be drained from the reactor, evaporated, condensed, and recycled; high cost	
Biological	Degrades lignin and hemicelluloses; low energy requirements	Rate of hydrolysis is very low	

Supply Chain Operations (mid-, short-term decisions)



Challenges with Biomass Supply Chains and Logistics Management

- Supply is constrained by availability
- Supply is seasonal and uncertain- multi-feed technology
- High logistics costs
- Widely dispersed physical distribution
- Bulky and difficult to transport
- High transport costs
- Biomass compositional changes with time ?

Lack of technical information on biomass Supply chain design & management is a very weak link

Biomass to Ethanol International Commercialization status



S.N	Name and Location	Year	Size	Technology IndianOil The Power of Ponihit
1.	Beta Renewables ,Crescention Italy	2014	20 MGY, Multi-feedstock	Prosea (Steam Explosion) Technology ,Novozymes
2.	Abengoa Bioenergy Hugoton,USA	2014	25 MGY, Multiple feedstock	Acid Pretreatment. Dyadic
3.	Poet-DSM, EMMETSBURG , IOWA	2015	25 MGY, Corn crop residue	Acid and Steam pre-treatment, DSM has enzymes and Yeast
4.	DuPont- Danisco	2015	30 MGY , Corn Stover	Pre-processing and Mild alkali. Accelerase enzymes from Genencor

Other 2nd Generation Ethanol Technology Providers



SI No.	Technology Provider	Key Features of Technology
1	DBT ICT centre, Mumbai	 Demo plant of 10 Tons/day from Biomass to ethanol based on ammonia and acid process followed by enzyme hydrolysis Biomass to ethanol conversion in < 18 hrs Low Capex and Opex, Viable at 250 tons/day scale. Cost of ethanol including capex depreciation is Rs 40/litre
2	Praj Industries, Pune	 First Indian technology developed in 2010 multiple feedstock based on acid Total Time from Biomass to ethanol in 80-90 hrs Cost of ethanol excluding capex depreciation is Rs 30-34/litre
3	Renmatix, USA	 Novel technology based on Supercritical hydrolysis of water Separates C5 , C6 and lignin fractions Investment of Rs 800 crores for 500 Tons/day biomass plant
4	Chempolis, Finland	 Multi-feed technology using formic acid to separate cellulose from hemicelluloses and lignin Most of the equipment used are standard pulp and paper equipment Cost of ethanol including capex depreciation is Rs 45/litre

Conclusion



- Production of 2nd generation ethanol is essentially required in India.
- Biomass feedstock could be an option to a country like India
- India has surplus availability of biomass which can be converted to ethanol.
- Cost economics is favorable at the current price of ethanol
- Ingenious technologies are also available but need to be established on commercial scale.
- Biomass supply chain need to be established for the sustainable supply
- Indigenous enzyme development & production would further make the technology economically favorable.
- 2nd generation Ethanol production would help to achieve 20% bio-fuels target of Bio-fuel policy.

Thank you



Composition some Indian feedstock's

Lignocellulosic materials	Cellulose (%)	Hemicelluloses (%)	Lignin (%)
Hardwood stems	40-50	24-40	18-25
Softwood stems	45-50	25-35	25-35
Nut shells	25-30	25-30	30-40
Corn cobs	45	35	15
Grasses	25-40	35-50	10-30
Paper	85-99	0	0-15
Wheat straw	30	50	15
Sorted refuse	60	20	20
Leaves	15-20	80-85	0
Cotton seed hairs	80-95	5-20	0
Newspaper	40-55	25-40	18-30
Waste papers	60-70	10-20	5-10
Solid cattle manure	1.6-4.7	1.4-3.3	2.7-5.7
Coastal Bermuda grass	25	35.7	6.4
Switch grass	45	31.7	12
Swine waste	6.0	28	na

Cellulose and hemicellulose content from 65-80% in biomass