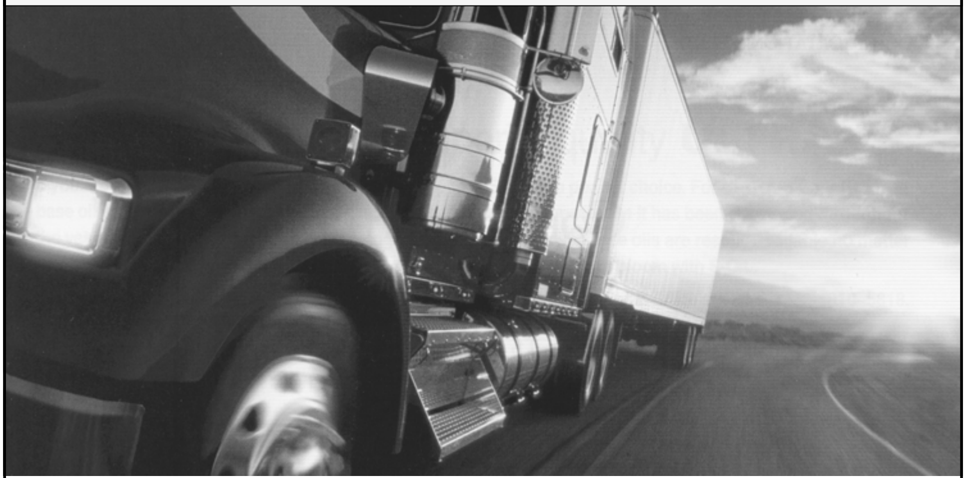
B I O G O R I V A



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Fakultet kemijskog inženjerstva i tehnologije
Sveučilište u Zagrebu

Fosilna goriva / Fossil Fuels
- Benzin / Gasoline
- Dieselsko gorivo / Diesel
- UNP / LPG
- Sintetska goriva / Synfuels - CTL & GTL
- Prirodni plin i SPP / Natural Gas & CNG

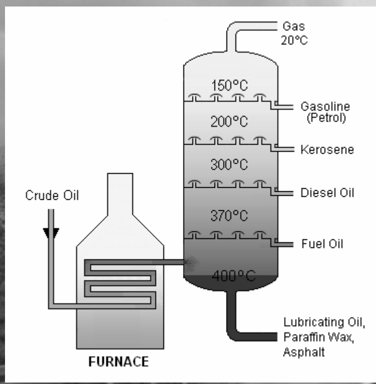
Obnovljiva goriva / Renewable Fuels
- Biodizel / Biodiesel (FAME)
- Obnovljivi dizel / Renewable Diesel (CH)
- Sintetska BTL goriva / Synthetic Fuel - BTL
- Bioetanol / Bioethanol
- Celulozni etanol / Cellulosic Ethanol
- Bio ETBE
- Bio MeOH & Bio DME
- Biobutanol
- Bioplin – biometan / Biogas
- BioVodik / BioHydrogen

Gasoline, Diesel, and LPG Technologies

In this section we will be describing the different refining technologies relating to Gasoline, Diesel and LPG.
Although these are labeled as conventional technologies, refineries today have become increasingly more efficient and efforts across the globe are being made to invest in better performing technologies and processes that save energy and decrease each refineries environmental impact whilst meeting increasingly more stringent fuel product specifications.

As can be seen below a basic refinery typically produces a variety of products including: LPG; petrochemicals; gasoline; jet fuel; paraffin for lighting and heating; lubricating oils, waxes and polishes; heavy fuel oil, and bitumen for roads and roofing.

Products Produced by Refineries



Different Refining Configurations Related To Automotive Fuel Qualities

A refinery's configuration refers to the type, size, number of process technologies and facilities employed, and the flow sequence.
Refinery configurations depend on what crude oil quality, product mix and quality, and environmental, safety, economic or other constraints were specified with its design. No two refineries are exactly alike, but refineries can be characterized into generic groups defined by the availability of the technologies.

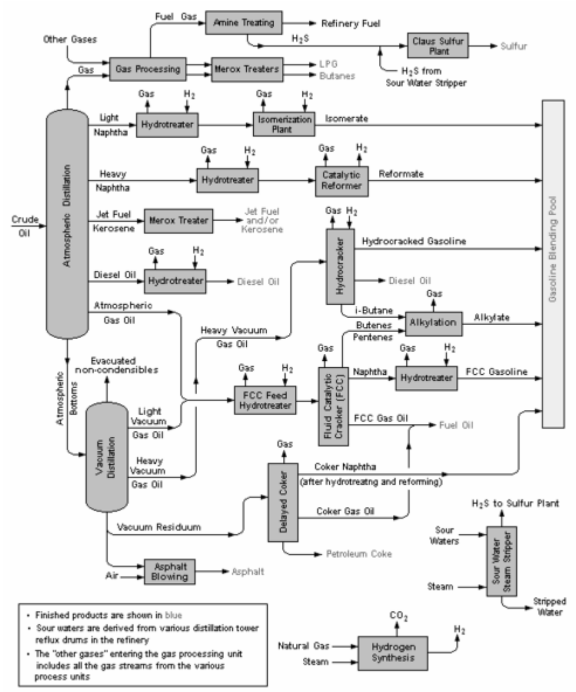
A refinery's complexity is typically referred to within four configurations.
These configurations are listed in the table below together with their available process technologies and their yields.

Refining Configurations and Their Yields					
Configuration Group & Process Technologies	**Product & Yield (vol %)**				**Comments**
	Gas	Gasoline	Diesel	Fuel Oil	
Topping • Crude Distillation	2	32	30	37	• Product quality and volume is dependent on crude oil source. • Distillate contains lots of heavy products. • Gasoline has low octane value.
Hydroskimming • Crude distillation • Hydrotreating • Reforming	3	28	30	37	• Product quality and volume is dependent on crude oil source. It allows refiners to adjust product slate (gasoline instead of naphtha). • Provides new possibilities to improve fuel quality, especially for gasoline. • Sulphur removal.
Conversion • Crude distillation • Hydrotreating • Reforming • FCC • Some upgrade units	3	49	30	17	• Flexibility in final production. • High quality products.
Deep Conv/Complex • Crude distillation • Hydrotreating • Reforming • FCC • Many upgrade units	3	47	43	4	• Addition of coking allows minimal production of low valued fuel oil.

Refineries are comprised of a number of individual technology based processing facilities with varying objectives, and integrated as necessary to meet product targets.
The types, size, number and flow sequence of a specific refinery (i.e., refinery configuration) will vary depending on crude oil quality, required product mix and quality, and environmental, safety, economic or other constraints.

[redacted]

All these steps and technologies are included in the figure below that illustrates a complex refinery configuration.



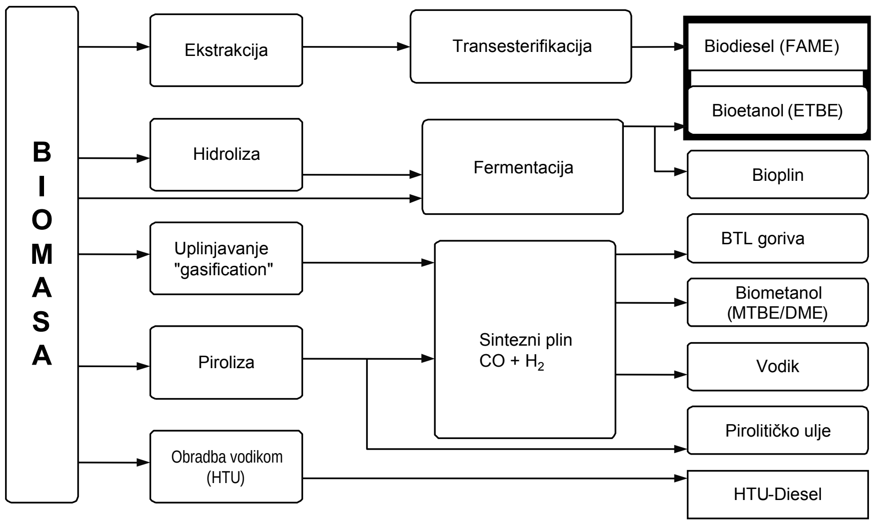
Refinery Flow Diagram

Ubrzani razvoj svjetskog gospodarstva prati stalan porast potrošnje goriva i petrokemijskih sirovina, što za krajnju posljedicu ima ubrzan iscrpak fosilnih goriva i povećanu emisiju stakleničkih plinova.
Uzrok je to sve veće nestabilnosti i izraženog porasta cijene nafte na svjetskom tržištu. Kao jedno od mogućih i prihvatljivih rješenja primjena je biogoriva zajedno s drugim alternativnim izvorima energije.

Biogorivo se najvećim dijelom upotrebljava kao gorivo za transport, a dobiva se iz mnogih agrokulturnih izvora. Dolazi u kapljevitom stanju kao bioetanol ili biodiesel ili plinovitom obliku kao bioplin (metan) ili vodik. Izravna su zamjena za postojeća benzinska i dieselska goriva, te se mogu koristiti u obliku smjesa s konvencionalnim mineralnim gorivima ili u čistom obliku za pokretanje automobilskih motora.

Biogoriva mogu "preskočiti" zapreke njihovom ulasku na tržište jer su <u>kompatibilna s konvencionalnim motorima</u> i <u>lako se namješavaju</u> s fosilnim gorivima (?!).
Nadalje, njihove su dobre karakterisitke da korištenje u većem ili manjem udjelu dovodi do <u>smanjene emisije štetnih plinova</u>: CO, CO_2, NO_x, kao i krutih ugljikovih čestica, te se izbjegavaju problemi onečišćenja tla i vode koji se inače javljaju upotrebom MTBE-a.

Također, u širem kontekstu primjena biogoriva omogućava dodatno upošljavanje radne snage i povećanje iskorištenja u poljoprivredno ekstenzivnijim područjima, a na taj način smanjuje se ovisnost o promjenljivom globalnom tržištu nafte.



Tehnologije dobivanja biogoriva

Prednosti uporabe biogoriva najvećim su dijelom strateške i ekološke:

1. smanjuju ovisnost o fosilnim gorivima
2. ekološki pogodni jer ne sadrže sumporove spojeve niti postojane aromatske ugljikovodike (benzen) izrazito štetne po okoliš
3. stvaraju znatno manje CO_2 i drugih stakleničkih plinova (biodiesel 40-60 %, etanol iz saharida do 55 %, iz celuloze do 80 %)
4. biorazgradljivost
5. visoka kvaliteta goriva (oktanski broj > 105, cetanski broj > 55)
6. mogu se odmah primijeniti jer nisu potrebne značajnije promjene na (standardnom motoru) niti na postojećoj distributivnoj infrastrukturi
7. značajnija uloga biogoriva na tržištu, potakla bi razvoj ruralnih sredina
8. moguće je provesti i decentraliziranu proizvodnju biogoriva na farmama i poljoprivrednim gospodarstvima

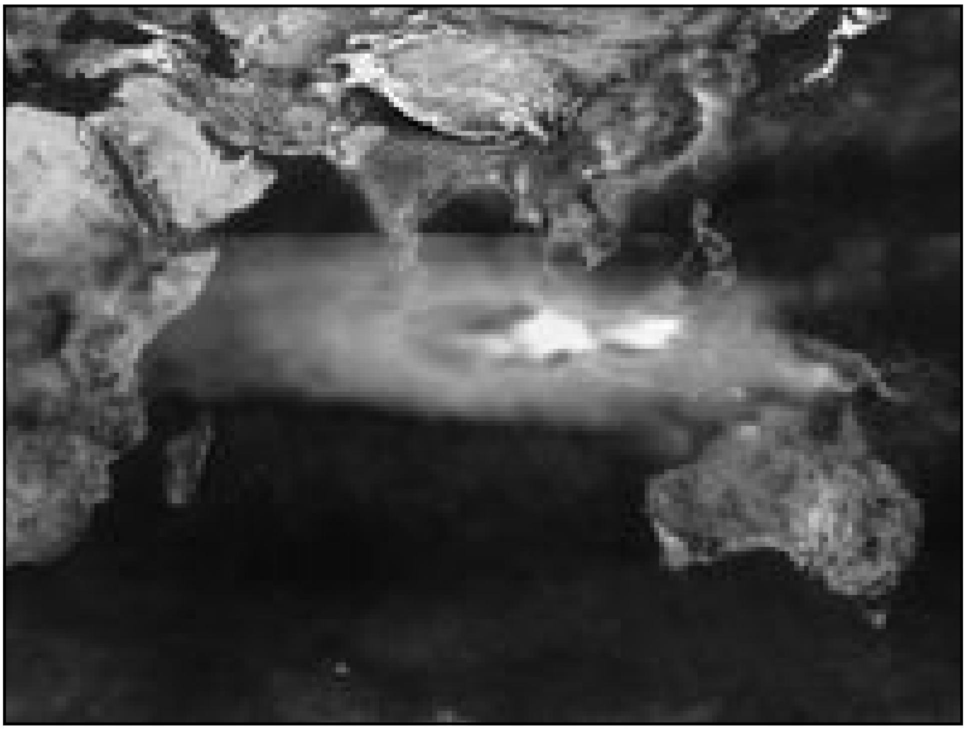
Potencijalne pogodnosti koje decentralizirana proizvodnja donosi samim korisnicima uključuju niže troškove, veću neovisnost, poboljšanu kvalitetu, racionalnije gospodarenje energijom, i doprinosi smanjenju potrošnje plina i električne energije.

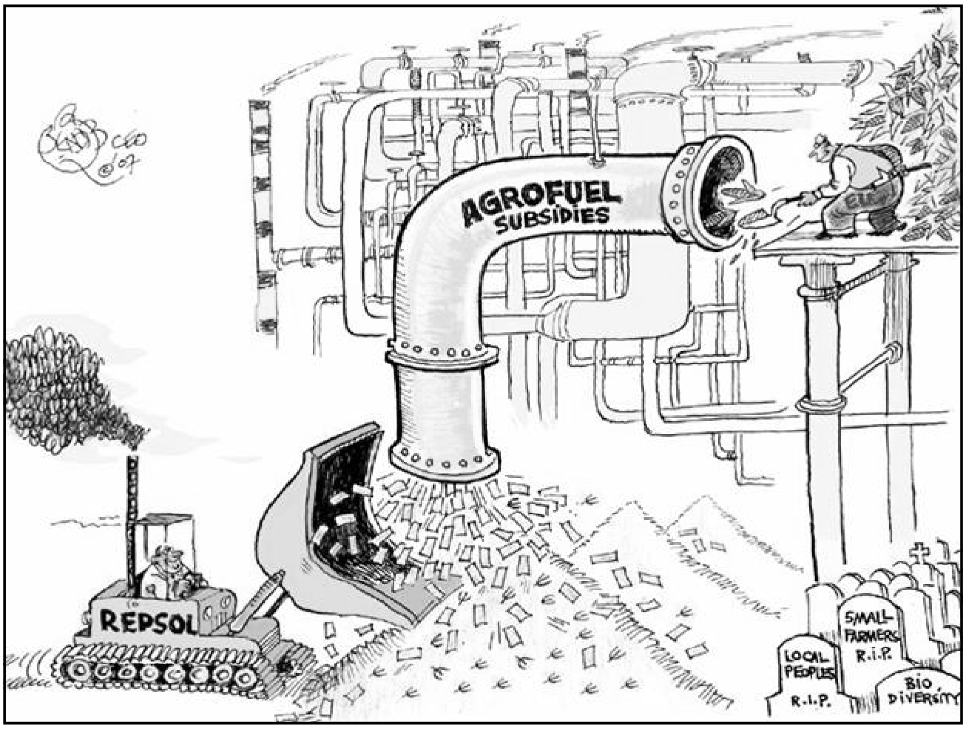
Nedostatci:

1. nastajanje monokultura / smanjenje biološke raznolikosti
2. prenamjena postojećih polja i površina pod šumama u svrhu sađenja onih kultura od kojih se proizvodi biogorivo
3. za konvencionalna biogoriva kao što su biodiesel i bioetanol, cijena proizvodnje znatno varira ovisno o vrsti sirovine
4. upotreba jestivih agrikultura za masovnu proizvodnju mogla bi imati negativan utjecaj na prehrambenu i poljoprivrednu industriju - cijenu hrane
5. povećanje upotrebe genetički modificiranih biljaka
6. zagađenost tla i voda uzrokovana intenzivnim uzgojem

(primjeri: SAD – Ohio, Brazil – Amazonija, Indonezija)

Gotovo 80 % od svjetske proizvodnje biodiesela je u Europi.
Proizvodnja biodiesela zahtjeva pet puta više obradivih površina po jedinici energije nego za proizvodnju bioetanola. Godine 2005. proizvedeno je 30 miliona tona bioetanola u svijetu, a samo 4 miliona tona biodiesela.




CEO
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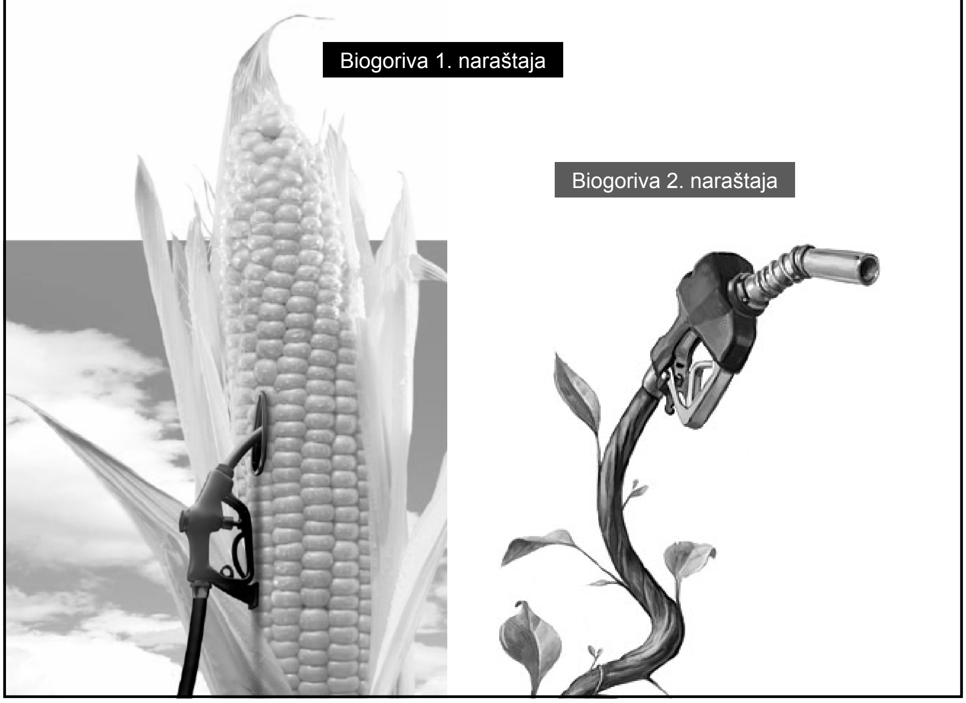
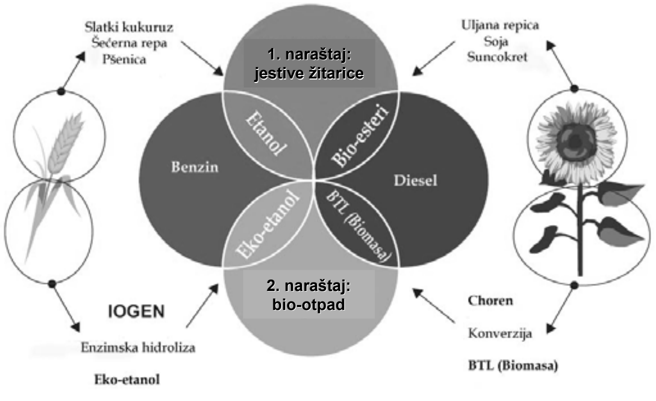
AGROFUEL
SUBSIDIES
REPSOL
SMALL-FARMERS R.I.P.
LOCAL PEOPLES R.I.P.
BIO DIVERSITY


THE CHANGING AMAZON
FROM THE MAGIC OF BIODIVERSITY...
...TO THE MONOCULTURE OF MAGGI!
TOCO TOUCAN
ARA PARROT
TAMA-RIN
3-TOED SLOTH
RUBBER TREE
MAHO-GANY
RHODO-DENDRON
PSILOSPO RANGIA FERN
SOY FUNDED by WORLD BANK IFC
SOY FUNDED BY CREDIT SUISSE
SOY RADO BANK
SOY UFJ BANK
SOY BNP PARIS
SOY ING BANK
SOY FORTIS BANK
HS BC
SOY BY BANCO ITA
NOTICE THE INCREDIBLE DIVERSITY OF FUNDING!

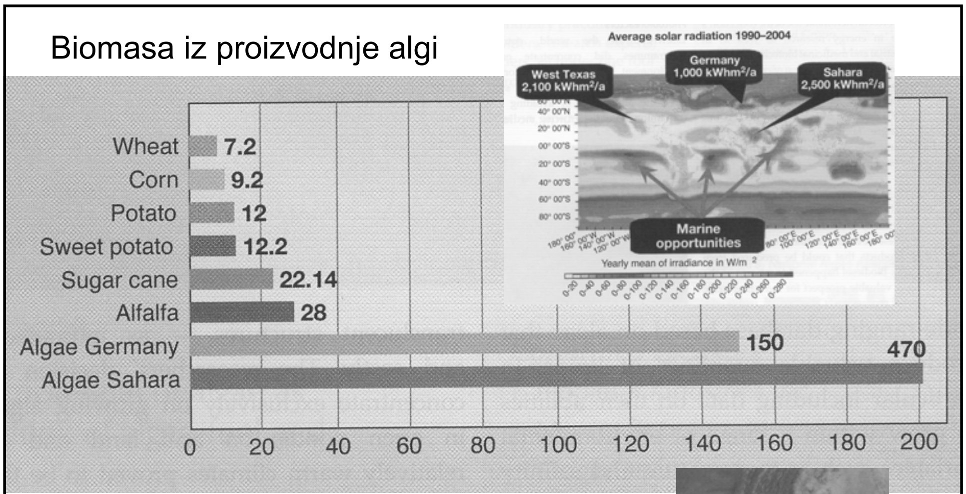


Alternativni postupci proizvodnje visoko kvalitetnih sintetskih goriva iz biomase = Fischer-Tropschova sinteza i biotehnološki postupci.

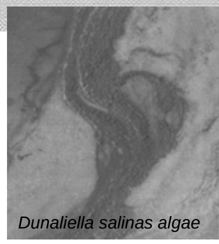


Stoga proizvodnja biodiesela, kao i sinteskog benzina iz biomase ima najveći potencijal jer kao osnovnu sirovinu koristi obnovljive izvore energije kao što su drvni otpad, otpad žitarica i bilo koji drugi otpad biološkog porijekla, pa čak i otpadni mulj. Te sirovine reagiraju s vodenom parom u prisutnosti katalizatora pri čemu nastaje sintezni plin, ugljikov monoksid i vodik, iz kojih se zatim dobivaju čisti kapljeviti CH, odnosno sintetska goriva i voda.

Biomasa iz proizvodnje algi

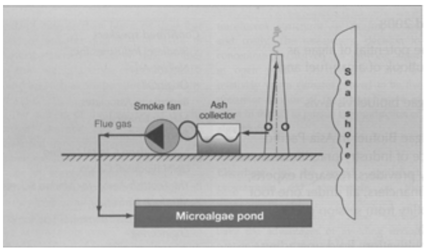


Iscrpak suhe biomase agrokulturnih usjeva (tona/hektar)



Dunaliella salinas algae

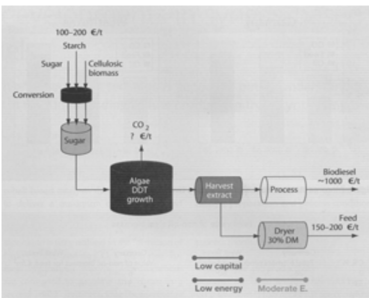
Tehnologijske sheme proizvodnje algi sa i bez sunčevog svjetla



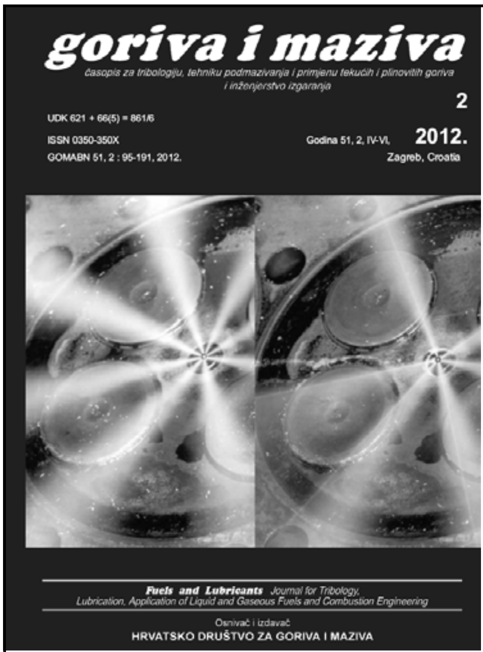
Economic comparison of various first- and second-generation biofuels process routes, including catalytic pyrolysis of biomass

	$/Boe	$/GJ
Crude Oil	60	10
Ethanol		
Sugarcane (Energy = biowaste)	54	9
Sugarcane (Energy = fossil)	90	15
Cellulose	120	20
Diesel		
Biodiesel from Jatropha	156	26
BTL via GTL	110	18
Bio-Crude (via direct BTL)		
Pyrolysis or Hydrothermal (HTU)	72	12
Catalytic Pyrolysis	60	10

Boe: Barrel of Oil equivalents GJ: Giga Joules



DDT – Deep Dark Tanks


goriva i maziva
časopis za tribologiju, tehniku podmazivanja i primjenu tekućih i plinovitih goriva i inženjerstvo izgaranja
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GOMABN 51, 2 : 95-191, 2012.
Zagreb, Croatia
Fuels and Lubricants Journal for Tribology, Lubrication, Application of Liquid and Gaseous Fuels and Combustion Engineering
Osnivač i izdavač
HRVATSKO DRUŠTVO ZA GORIVA I MAZIVA


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GOMABN 51, 3 : 192-285, 2012.
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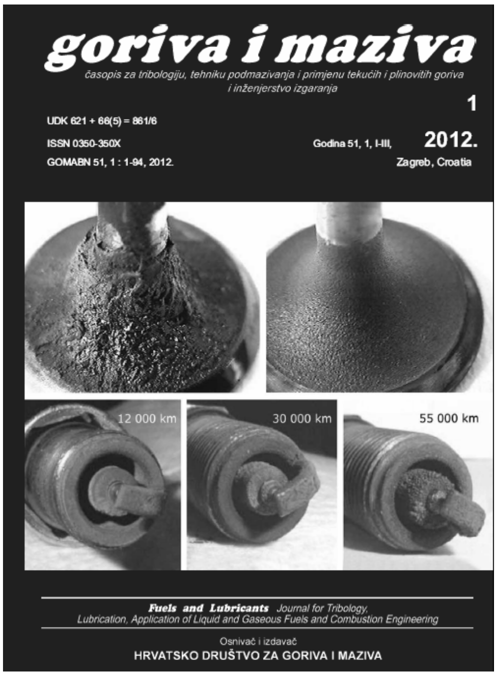
INA
Vi ste naša energija
Fuels and Lubricants Journal for Tribology, Lubrication, Application of Liquid and Gaseous Fuels and Combustion Engineering
Osnivač i izdavač
HRVATSKO DRUŠTVO ZA GORIVA I MAZIVA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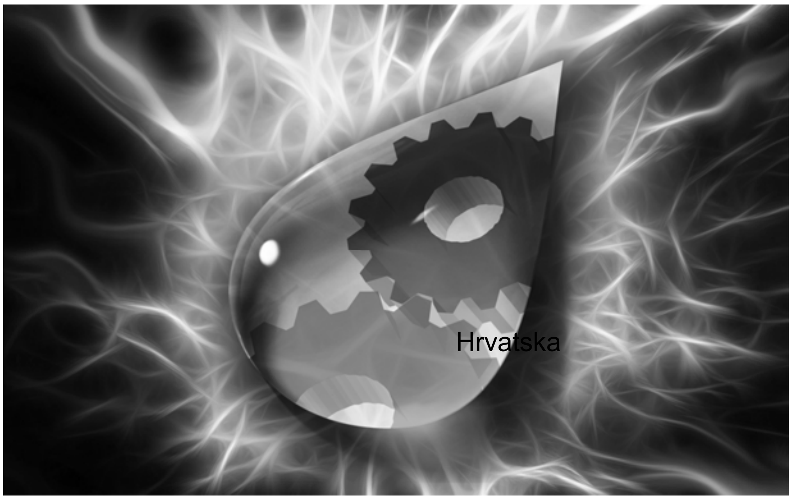


46. međunarodni simpozij
Hrvatskog društva za goriva i maziva

GORIVA I MAZIVA

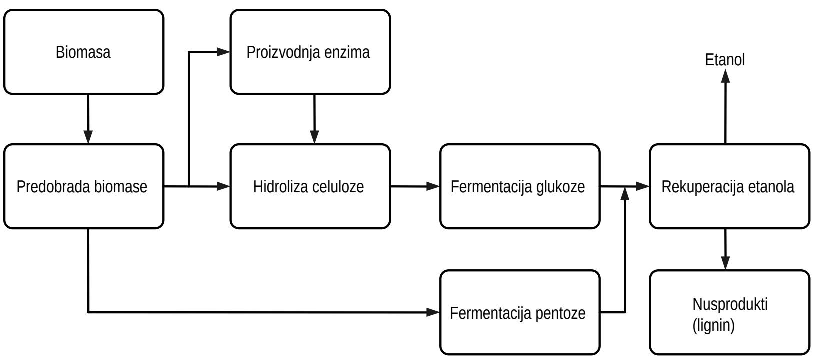
16.-18.10.2013. Poreč

GOMA

Hrvatsko društvo za goriva i maziva
Berislavićeva 6, HR-10000 Zagreb
tel: +385 (0)1 4873 549 - fax: +385 (0)1 4872 503
e-mail: goma@goma.hr - www.goma.hr

Etanol je biogorivo koje se danas najviše upotrebljava (3 % od ukupne svjetske upotrebe transportnih goriva) s tim da se 10 % rabi za namješavanje s klasičnim gorivom zbog povećanja oktanskog broja benzina.

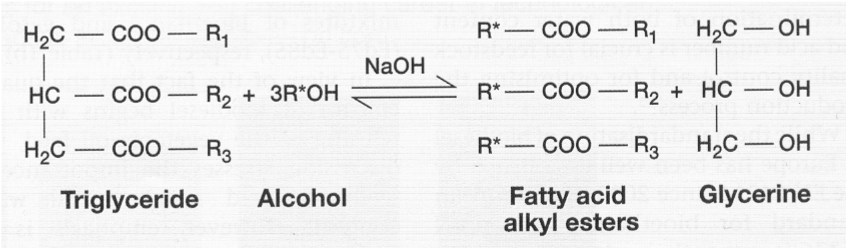
Konvencionalna proizvodnja etanola iz kukuruza i šećerne melase dobro je poznata i razvijena tehnologija. Bioetanol se može proizvesti i iz ostataka žetve, konverzijom celuloze u šećer te procesom fermentacije u alkohol. Upotrebom celuloznih sirovina kao što su slama, drvni otpad, itd., proizvodnja bioetanola nema utjecaja na proizvodnju hrane, ali je proces u razvitku i traže se rješenja za ubrzavanje reakcije hidrolize i zbrinjavanje nepoželjnih sporednih produkata.



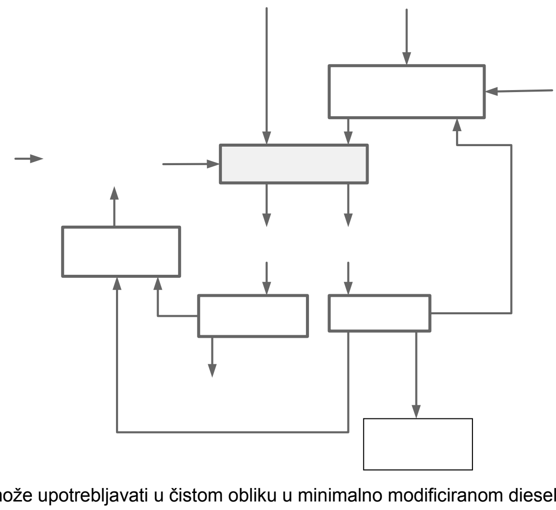
Dobivanja bioetanola procesom fermentacije

Biodiesel (alkilni esteri viših masnih kiselina) je čišće i ekološki povoljnije gorivo koje može zamijeniti klasično dieselsko gorivo za pokretanje motora automobila.

Može se proizvesti iz prirodnih obnovljivih izvora kao što su biljna ulja i životinjske masti. Masti i ulja kemijski reagiraju s alkoholom (uglavnom metanolom) da bi se proizveli metilni esteri viših masnih kiselina, poznati kao biodiesel, pri čemu se kao koproizvod u procesu dobiva glicerol.



Proces dobivanja biodiesela



Biodiesel se može upotrebljavati u čistom obliku u minimalno modificiranom dieselskom sustavu s kompresijskim paljenjem, ali najviše se još uvijek upotrebljava u smjesi s klasičnim dieselskim gorivom.
Gotovo 80 % od svjetske proizvodnje biodiesela je u Europi. Proizvodnja biodiesela zahtjeva pet puta više obradivih površina po jedinici energije nego za proizvodnju bioetanola.
Godine 2005. proizvedeno je 30 miliona tona bioetanola u svijetu, a samo 4 miliona tona biodiesela.

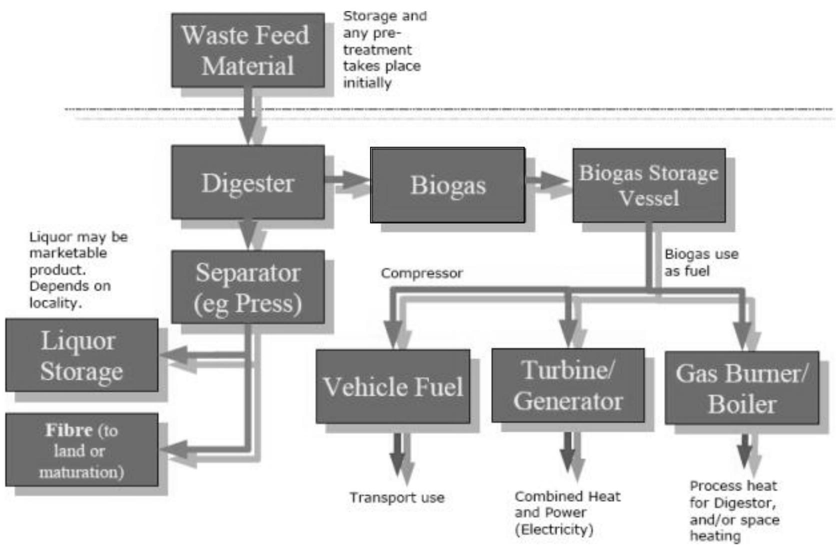
Biogas / Bioplin (metan)

Biogas can be extracted from sewage treatment plants, refuse dumps and other sources of biologically degradable material. The fuel can also be produced by biomass gasification. A variety of process schemes have been developed.

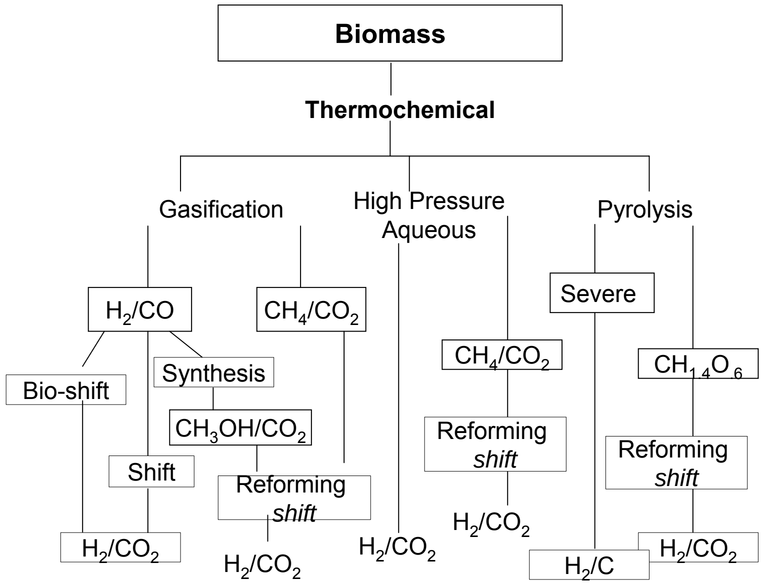
Biogas is a gas mixture: approximately 40-75% CH_4, 25-60% CO_2, 2% of other gases (hydrogen, hydrogen sulphide and carbon monoxide).

Biogas develops through anaerobic fermentation.
During this process, organic substances are decomposed by micro-organisms.
The substances added to the system produce the biogas in an oxygen-free environment.
In the first step, the organic substances are divided into molecular components (sugar, amino acids, glycerine and fatty acids).
Microorganisms convert these intermediate products into hydrogen and carbon dioxide, which are then transformed into methane and water according to the equation:

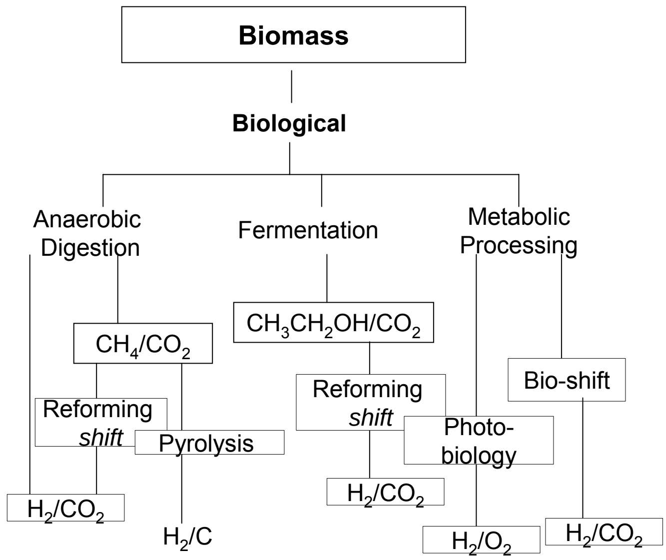
$$CO_2 + 4H_2 \dashrightarrow CH_4 + 2H_2O$$



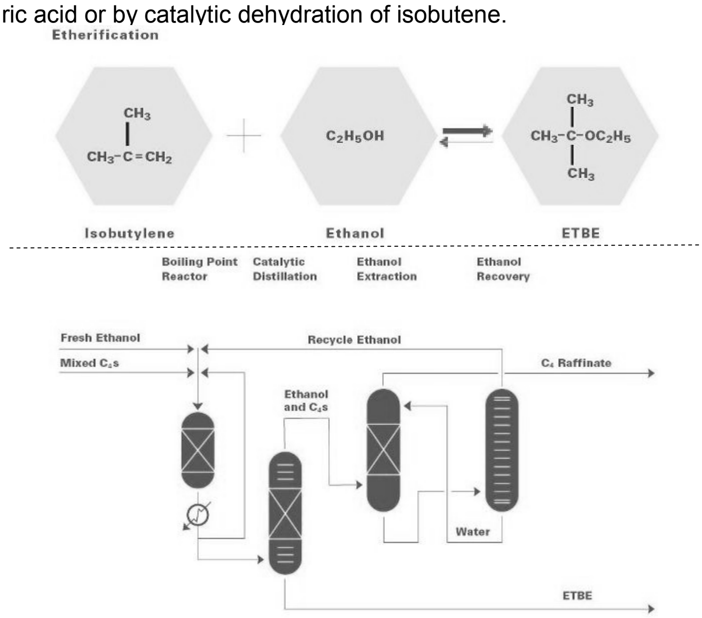
Dobivanje vodika iz biomase



Dobivanje vodika iz biomase

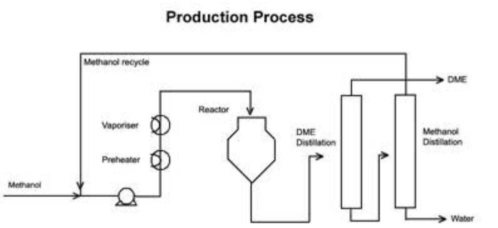


Bio-ETBE is produced by mixing bio-ethanol (47%v) and isobutylene (53%v) in the presence of a catalyst. Isobutylene can be isolated from refinery streams by reaction with sulfuric acid or by catalytic dehydration of isobutene.



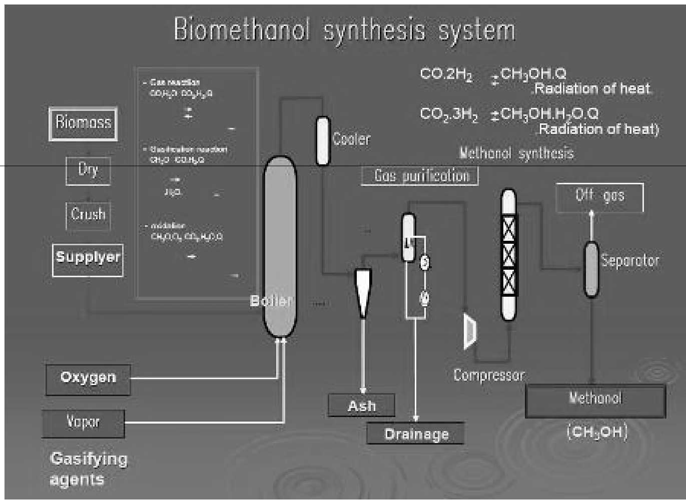
Bio-DME (C_2H_6O) is a colourless, gaseous ether that can be used in diesel and gasoline engines and in gas turbines. It works particularly well in diesel engines because of its high cetane number.

DME can be processed and produced from natural gas, coal and biomass. Currently there are two ways to produce DME: one is methanol dehydration and the other is DME synthesis from syngas. With the catalytic dehydration method, DME is produced from two methanol molecules in the presence of a catalyst, which produces one DME molecule and water.

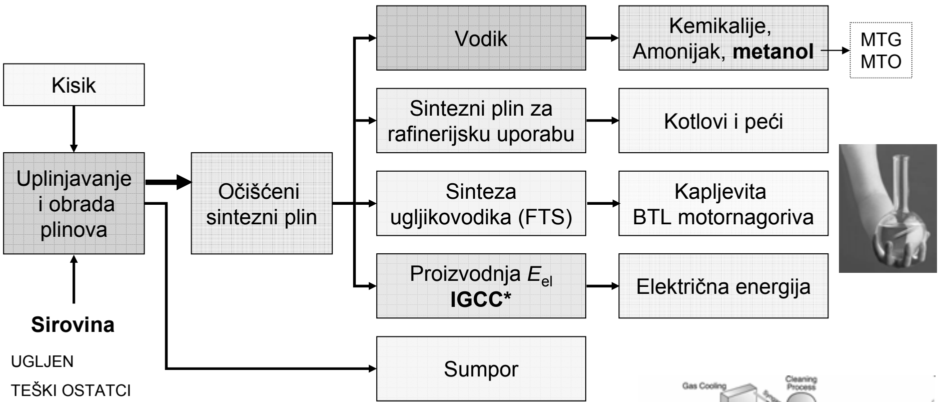


Bio-methanol (CH_3OH) is an alcohol that can be used in a blend with conventional (fossil) gasoline as a substitute for gasoline.

Bio-methanol can be produced naturally by the anaerobic metabolism of many types of bacteria. Methanol can also be produced synthetically by using natural gas. Natural gas and steam are reformed to produce CO and H_2 in a furnace and the two then react to an added catalyst and produce methanol.



Objedinjavanje preradbe nafte, petrokemijske proizvodnje i proizvodnje energije u modernim rafinerijama na temelju procesa uplinjavanja
sintezni plin (H_2+CO), petrokemikalije (CH_3OH, NH_3,…),
sintetički benzin i dieselsko gorivo, toplinska (para) i električna energija



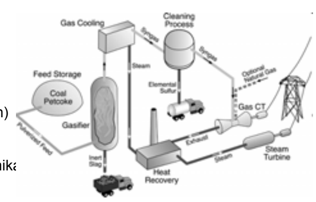
UGLJEN

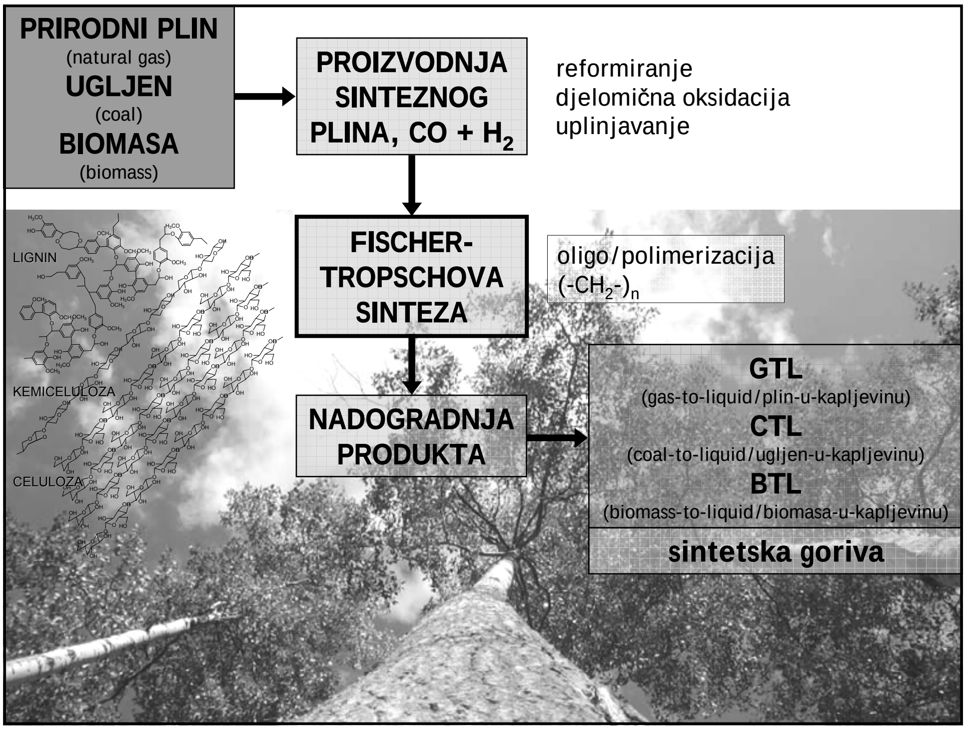
TEŠKI OSTATCI PRERADBE NAFTE

PRIRODNI PLIN

BIOMASA

***IGCC**
- zrelost tehnologije nije postignuta (komercijalna postrojenja od 1990-tih)
- visoka početna ulaganja
- nepouzdanost - neispunjena očekivanja učinkovitosti i ekonomičnosti
- standardizacija dizajna postrojenja; sirovina, poligeneracija: H_2, *E*, kemik
- zbrinjavanje CO_2
- 2015. - 2025. drugi naraštaj IGCC; > 500 MW_e (iz koksa)





BTL Diesel / SunDiesel

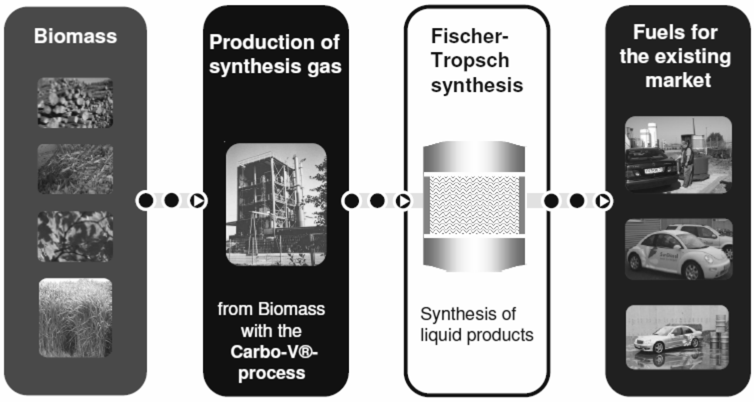
CHOREN

- reduces dependence on imported oil;
- is renewable and largely CO_2-neutral;
- can be produced and consumed locally and therefore creates a future for rural regions;
- can be directly fed into the infrastructure of existing distribution channels and is suitable for long-distance transportation and storage;
- can be used in existing engines, but can also be further developed for more sophisticated engines;
- has a high energy density (40 MJ per liter);
- is an extremely clean automotive fuel: no sulfur and no aromatic hydrocarbons;
- causes significantly fewer exhaust gas emissions than traditional fossil fuels;
- can be manufactured from a very broad range of feed materials;
- has a high yield/ha

What is SunDiesel?

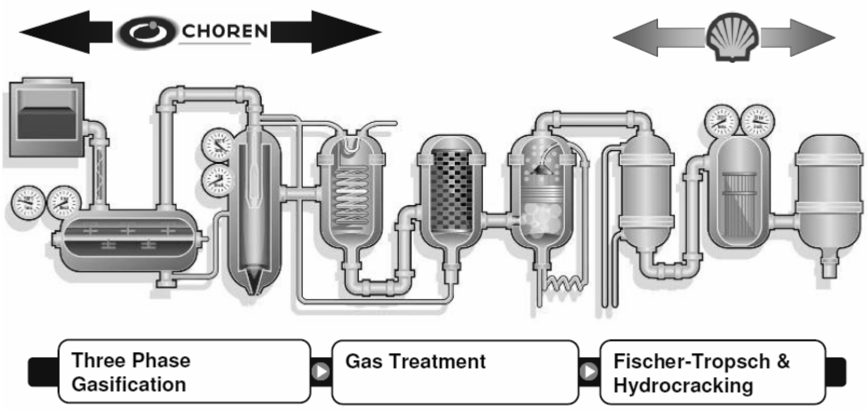
CHOREN

Production process

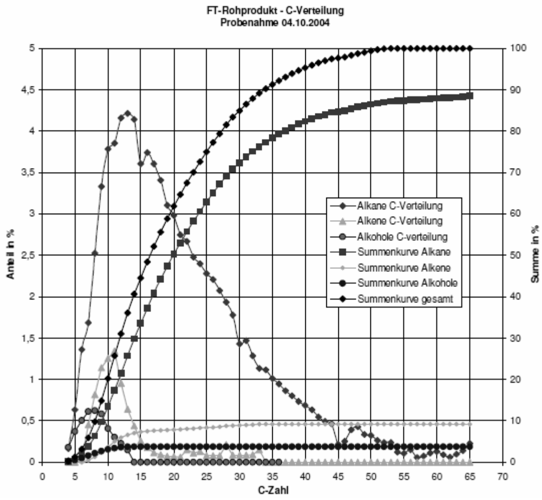


The BTL process

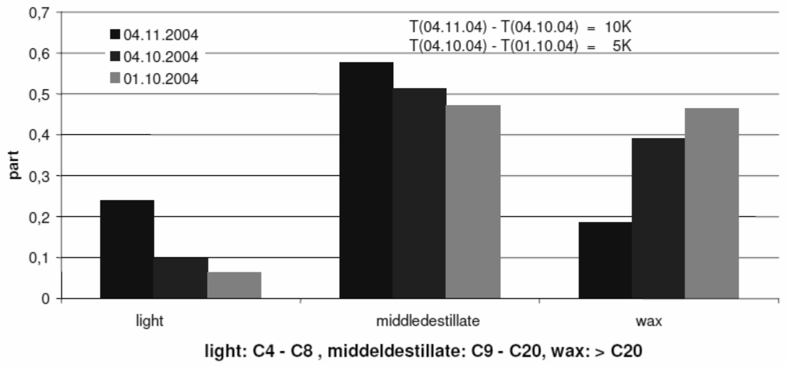
CHOREN



CHOREN FT- raw product (example)



FT raw product = f (temperature)



Fuel Properties

CHOREN

General

- Sulphur: zero (<< 10 ppm)
- Low aromates
- High H/C-ratio
- Low density

Diesel

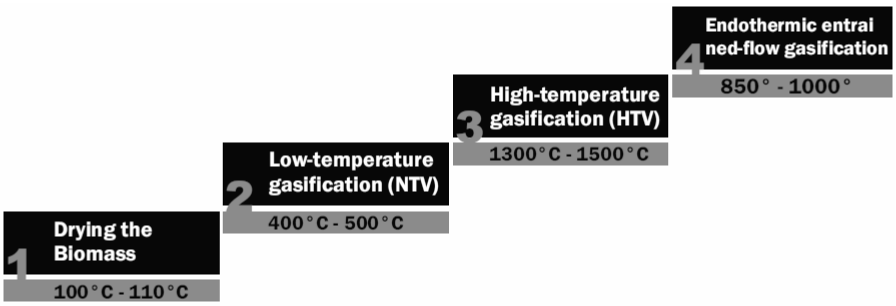
- High Cetane No.: > 60

Naphtha

- Diesel-like Cetan No. at low boiling range:

=> good opportunities for HCCI/CCS-systems

The **Carbo-V® Process** is a **multi-stage gasification process** involving the following **PROCESS STEPS**:

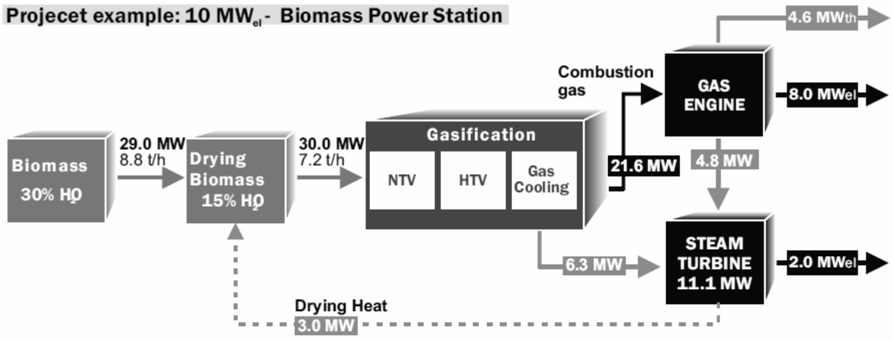


Start-up of the first commercial BTL production facility

CHORENs BETA-Plant Freiberg

ENERGY STATEMENT AND DEGREES OF EFFICIENCY

Projecet example: 10 MW_{el} - Biomass Power Station



Input - Output

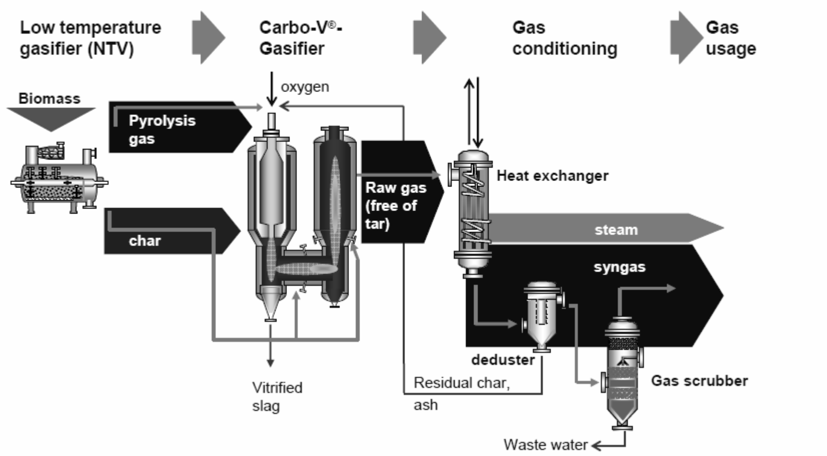
Biomass	=	29.0 MW
Other fuels	=	0.2 MW
Electricity required	=	0.8 MW
Total input	=	30.0 MW
Electricity output	=	10.0 MW
Heat output	=	4.6 MW

Net Degree of Efficiency

Cold gas	=	72.0%
Electrical	=	33,3%
Therminal	=	15,3%
Total	=	48,7%

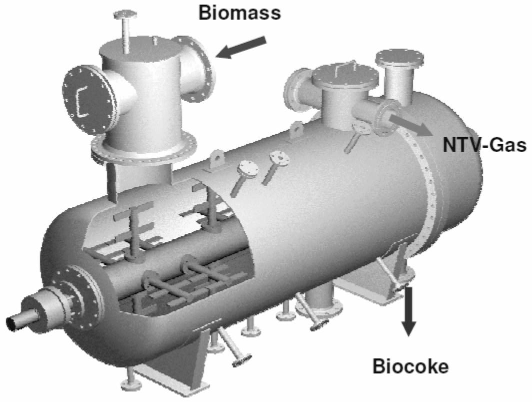
The Carbo-V® Process

CHOREN



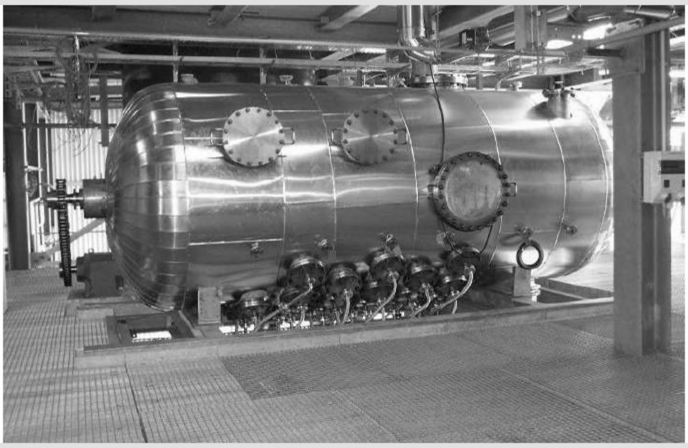
Low Temperature Gasification (NTV) Pyrolysis

CHOREN



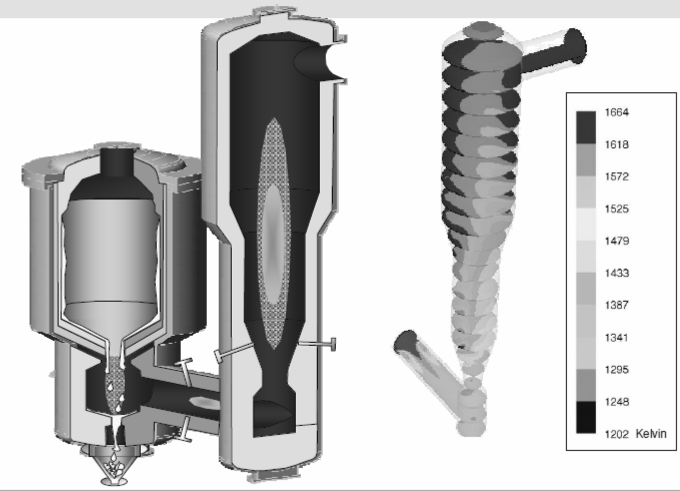
Low Temperature Gasification (NTV) Pyrolysis

CHOREN



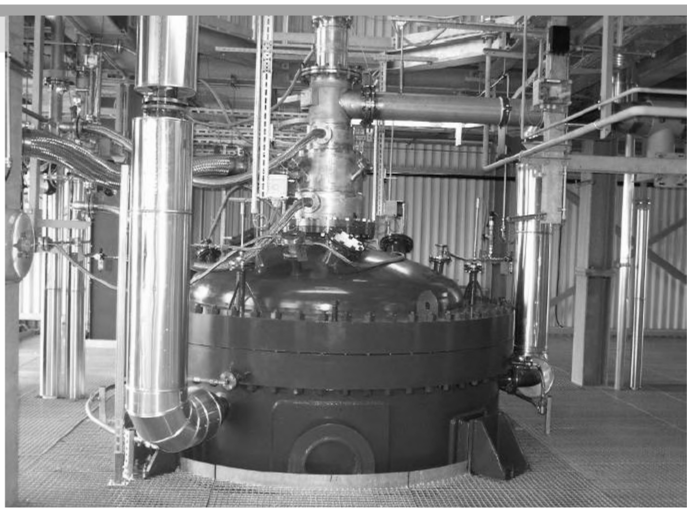
High Temperature Gasification (HTV)
Tar Oxidation and endothermic quench

CHOREN



High Temperature Gasification (HTV)
Tar Oxidation and endothermic quench

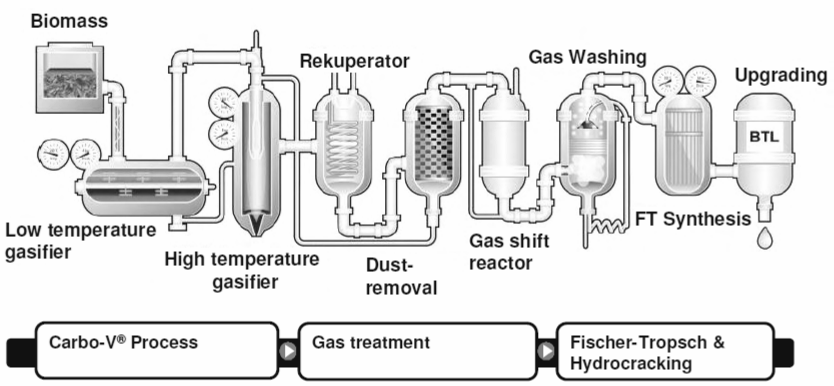
CHOREN



BTL production

CHOREN

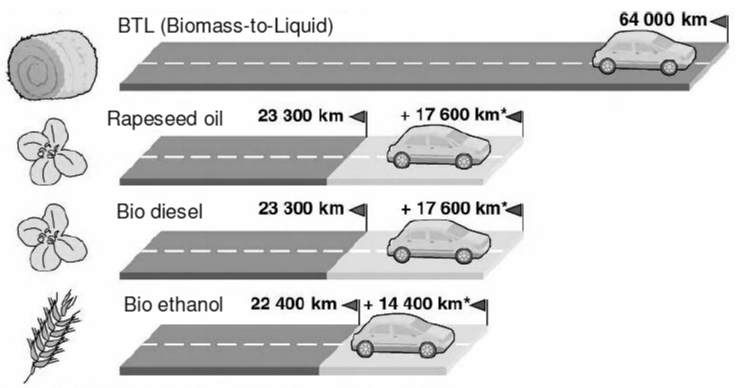
From Biomass to BTL



Comparison of Bio Fuels

CHOREN

The Distance a car can reach filled with Bio Fuels from 1 ha acreage



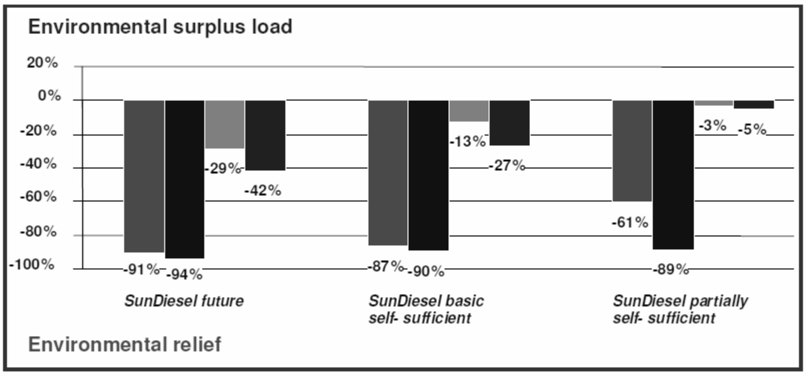
Automotive Fuel Consumption: Otto 7.4 l / 100km, Diesel 6.1 l/100km

Source: Fachagentur Nachwachsende Rohstoffe e.V. FNR

Effects on the environment

CHOREN

Using BTL instead of fossil diesel

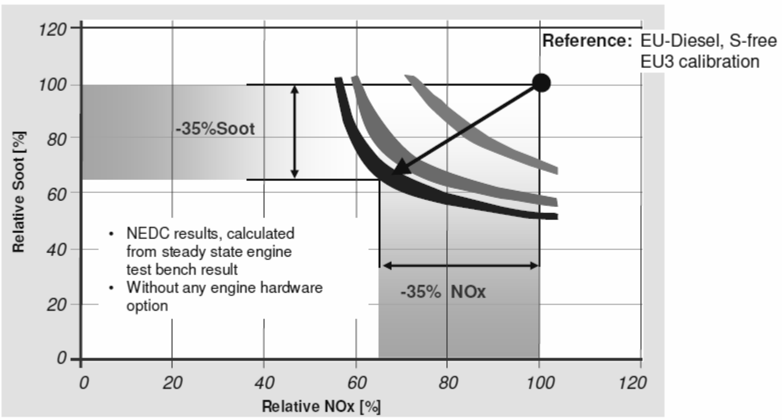


- greenhouse gases potential [kg CO2-equivalent]
- photo-oxidations potential [kg ethene-equivalent]
- eutrophication potential [kg phosphate-equivalent]
- over-acidic potential [kg SO2-equivalent]

NO_x-Soot Trade-Off

CHOREN

GTL blending effects



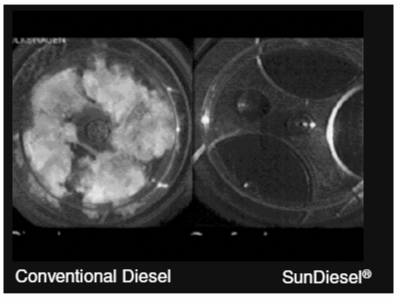
Source: *DaimlerChrysler, P. 11, Fig. 8*

GTL *EU50-GTL50* *EU80-GTL20*

SunDiesel® – *made by CHOREN*

CHOREN

- can be directly fed into the existing infrastructure
- can be used in existing engines, but also in more sophisticated engines
- is renewable and largely CO_2-neutral
- is extremely clean: no sulphur and no aromatic hydrocarbons
- has a high cetane number
- causes significantly fewer exhaust gas emissions than traditional fossil fuels
- has a high yield/ha
- has a high energy density (40 MJ per litre)



Beta-Plant Freiberg: BTL Production in Industrial Scale

CHOREN

1 Biomass conditioning | 2 Biomass storage | 3 Biomass dryer | 4 Carbo-V® gasifier | 5 Power station | 6 Gas conditioning & Fischer-Tropsch synthesis | 7 Compressor building | 8 Storage for offsite & utility gases

Višestupnjeviti proces:
1. Sušenje biomase
2. Niskotemperaturno uplinjavanje, 400-500 °C
3. Visokotemperaturno uplinjavanje, 1300-1500 °C
4. Endotermno uplinjavanje, 850-1000 °C

- 45 MW thermal
- 65,000 t_{DM}/a feedstock
- 18 Million Liter BTL

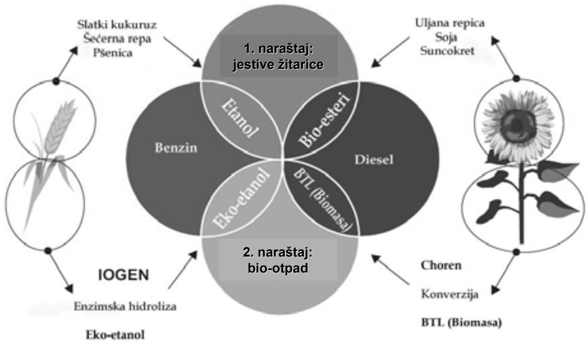
Obnovljivi diesel (Renewable Diesel)

Proizvodnja dieselskog goriva vrhunske kvalitete iz obnovljive bio-sirovine.

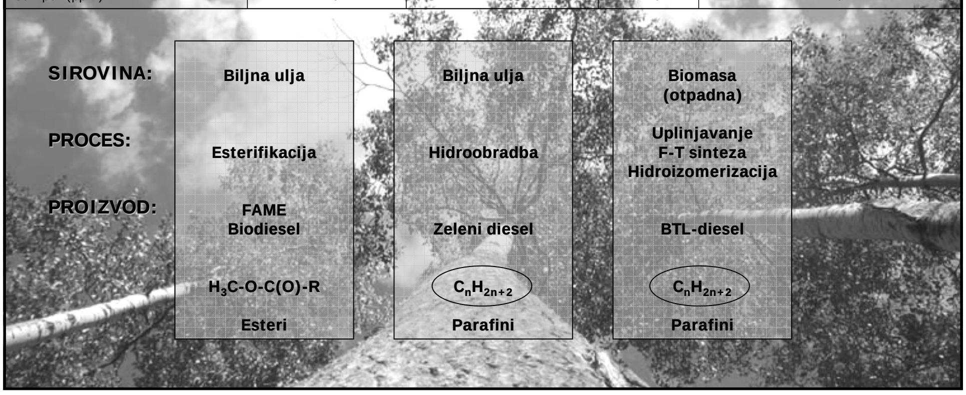
"Biodiesel (FAME)" = transesterifikacija biljnih ulja i masti.

"Zeleni diesel" = katalitička hidrokonverzija smjese dieselskih frakcija i biljnih ulja u rekatoru za hidroobradbu pri visokim temperaturama i visokom tlaku vodika.
Trigliceridi iz biljnih ulja ili životinjskih masti prevode se u linearne i izomerizacijom u granate ugljikovodike koji čine dieselsko gorivo upotrebljivo u nepreinačenim motorima s unutarnjim izgaranjem.

"BTL-diesel" = proizvodi se postupkom "biomasa-u-kapljevinu" (Biomass-to-Liquid), višestupnjevitim procesom: uplinjavanje / Fischer-Tropschova sinteza / hidroobradba.



Svojstvo goriva	Biodiesel: FAME	Zeleni Diesel	BTL-Diesel	Mineralni / Fosilni Diesel (EN 590)
Gustoća pri 15 °C (kg/m³)	885	775 - 785	770 - 785	835
Viskoznost pri 40 °C (mm²/s)	4.5	2.9 - 3.5	3.2 - 4.5	3.5
Cetanski broj	51	84 - 99	73 - 81	53
Destilacija 10 vol. % (°C)	340	260 - 270	260	200
Destilacija 90 vol. % (°C)	355	295 - 300	325 - 330	350
Točka zamućenja (°C)	-5	- 5 to -30	0 to -25	-5
Niža ogrjevna vrijednost (MJ/kg)	38	44	43	43
Niža ogrjevna vrijednost (MJ/l)	34	34	34	36
Poliaromati (mas. %)	0	0	0	8
Kisik (mas. %)	11	0	0	0
Sumpor (ppm)	<10	0	<10	<10



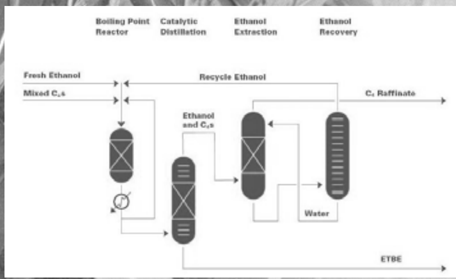
SIROVINA:	**Biljna ulja**	**Biljna ulja**	**Biomasa (otpadna)**
PROCES:	**Esterifikacija**	**Hidroobradba**	**Uplinjavanje F-T sinteza Hidroizomerizacija**
PROIZVOD:	**FAME Biodiesel**	**Zeleni diesel**	**BTL-diesel**
	H_3C-O-C(O)-R	**C_nH_{2n+2}**	**C_nH_{2n+2}**
	Esteri	**Parafini**	**Parafini**

Bio-oksigenati motornih benzina

Proizvodnja Bio-ETBE, sastavnice i poboljšavala oktanskog broja motornih benzina.

Bio-ETBE ($C_6H_{14}O$) = katalitička esterifikacija bio-etanola (47 vol. %) i izobutilena (53 vol. %). Izobutilen se može izdvojiti iz rafinerijskih tokova i dodatno proizvesti katalitičkom dehidrogenacijom izobutana.

Bio-ETBE, za razliku od etanola, nije mješljiv s vodom.



Z A K LJ U Č N O

- široki raspon zamjenskih obnovljivih goriva prema kemijskom sastavu, svojstvima, tehnologijama proizvodnje
- nužan stručno usmjeren i interdisciplinaran pristup u kreiranju energijskih strategija u skladu s postojećim resursima (zalihe fosilne i bio sirovine, postojeća industrija, infrastruktura…) i obvezujućim / nametnutim ? / zakonodavstvom (CO_2, obnovljivi izvori…)


Hvala na pažnji !