The use of corn oil for biodiesel production

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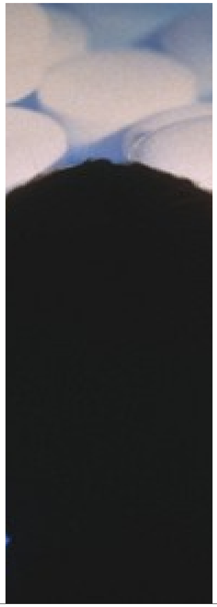

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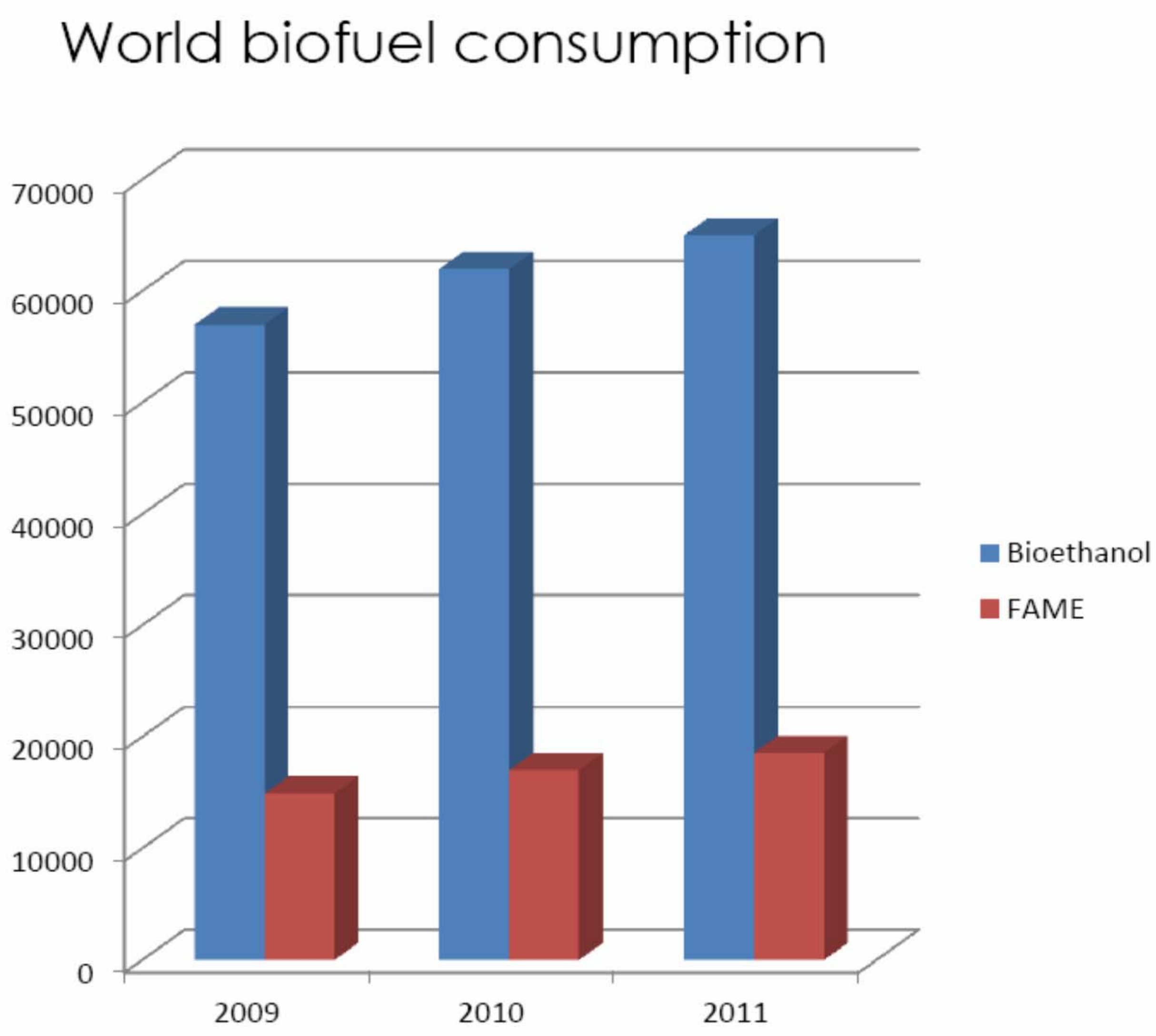

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Source:Kingsman

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Feedstocks for biofuels production

- **Primary oil** for biofuel production: rapeseed, soya, sunflower, palm – conflict with food production.
- **Secondary oil** for biofuel production:

- low quality animal fat (tallow, lard, chicken,..)

- side stream and waste cooking oils,

- oils form industrial crops (jatropha, algae,..)

Corn – the raw material for production of fuels

- Corn is an important raw material for bioethanol production.
- On average, contains 71% starch, 12% protein, 3% sugar, 1.7% cellulose and 2-3% oil.
- The oil is contained in the germ of the grain.
- Up to 70% of corn is used as an animal feed, 20% for food, 5% in industry.
- Industrial use of corn is expanding
- By-product of bioethanol production -DDGS (Distillers dried grains with solubles) is used for the production of animal feed.

Corn germ oil - production

- Corn oil can be produced from germ separated in preparation of maize grains for fermentation or for production of starch.
- This procedure requires a higher initial investment and most bioethanol plants do not use this technology.

Parameter	Corn germ	Sunflower	Soya	Rapeseed
C16:0 (wt.%)	11,3 – 15,8	6,2 – 7,3	9,6 – 11,6	4,1 - 5,5
C18:0 (wt.%)	2,0 – 2,5	3,4 – 4,7	3,4 – 4,6	0,9 - 2,1
C18:1 (wt.%)	22,9 – 31,0	20,3 – 30,8	20,4 – 27,0	45,4 - 61,0
C18:2 (wt.%)	51,8 – 58,9	56,6 – 66,3	48,4 – 54,9	16,2 - 28,2
C18:3 (wt.%)	0,3 – 1,9	0,2 – 1,8	0,2 – 1,4	9,0 - 13,0
Iodine number (g I_2/100 g)	103 – 128	125 – 136	120 - 140	97 - 108
$Density_{15°C}$ (kg m^{-3})	922 – 926	922 – 926	924 – 928	913 - 918

Corn oil from bioethanol side products

- The second approach is the separation of lipids from side technology stream in bioethanol plant.
- Corn oil is in a fermentation product in three different forms: as a
- "free oil - FO," which can be separated by centrifugation, as
- „trapped oil - TO", which can be separated by extraction with n-hexane and as
- „bound oil - BO," which can not be separated by extraction with n-hexane. For the release of oil is used acid hydrolysis, hydrolysis with the enzymes or finer grinding of raw materials in preparation feed for fermentation.

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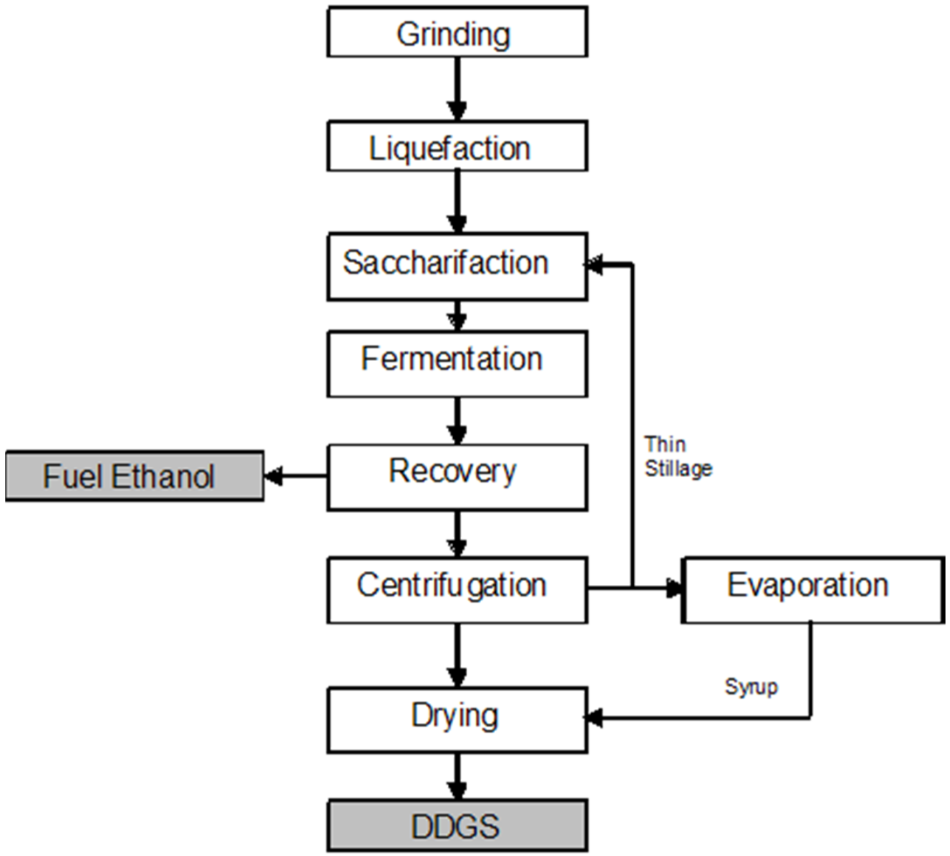
Dry grinding ethanol process scheme



Adapted from McAloon, A.; Tayor, F.; Yee, W.; Ibsen, K. and Wooley, R. (2000). Determining the Cost of Producing Ethanol from Corn Starch and Lignocellulosic Feedstocks. NREL/TP-580-28893.

Corn oil from whole stillage - extraction

- Compared with commercial corn germ oil extracted oil contains a higher proportion of free fatty acids.
- This corresponds to the high acid number 19.9 mg KOH / g. Corn oil contains the highest proportion of linoleic acid, oleic acid and palmitic acid.
- Although the absolute values vary, the ratio of oleic acid to linoleic acid is in a narrow range of values from 0.49 to 0.52.
- It is evident that the fermentation process forms free fatty acids from TAG

TAG profile	Extraction whole stillage, %
C12:0	0,01
C14:0	0,03
C14:1	0,01
C16:0	9,86
C16:1	0,04
C18:0	0,91
C18:1	18,93
C18:2	37,92
C18:3	1,47
C20:0	0,29
C20:4	0,24
C22:0	0,10
C22:1	0,04
C24:0	0,15
Acid number, mg KOH/g	19,91
Free fatty acids, % wt	13,7
Free sterols, % wt.	0,8

Processes to enhance oil recovery

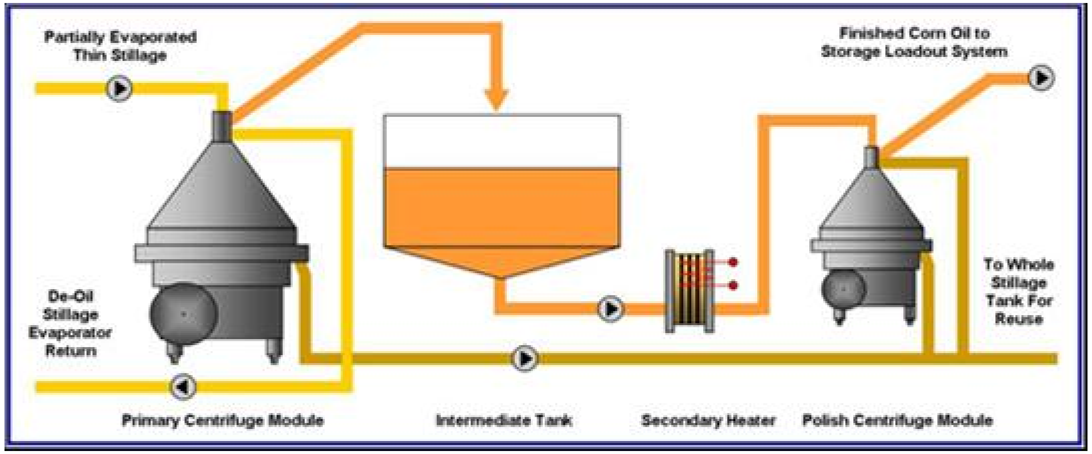
- Oil recovery by centrifugation of the liquids is generally viable method.
- Using polar solvents as an IPA and butanol achieved greater, 80% recovery.
- Increasing temperature to about 60ºC increased oil recovery (heat can break oil-water emulsion).
- By enzymatic treatment, 70% oil distribution was achieved in the thin stillage, compared to the conventional fermentation

S.Majoni et al.: J. Am. Chem. Soc. (2011) 88:425-434
H.Noureddini et al.: J. Am. Chem. Soc. (2009) 86:83-91

Corn oil - the technological processes -1

- GreenShift Corporation Company uses three phase -centrifuge for light stillage, and separates about 30 litres of oil on 1000 litres of alcohol.
- This provided light stillage shall be conducted in the evaporator and the concentrated syrup is feed to three-phase separation centrifuge (an additional 30 litres of oil).
- The company published the possibility of production of 7800 m^3 of oil in the production of 120 000 m^3 of bioethanol.
- GreenShift is owner of 5 main US patents – 8168037, 8008516, 7608729, 7601818, 79355840.
- In the near future we can expect further publication of patent applications, particularly in the USA.
- Using a mixture of enzymes and bacteria applied to the stillage will be released presented corn oil, which was further separated by known extraction procedures. Corn oil is largely emulsified ingredients, which include eg. phospholipids, waxes, glycolipids and others.

Corn oil - the technological processes - 2



- The process of Solution Recovery Services called ® COSS (Corn Oil Separation Services) is based on the separation of oil fraction from partially concentrated light stillage.
- In the second stage is oil clarified in the second decanting centrifuge. Oil yield is 25-30% oil which is present in DDGS, which is 2700-3300 m^3 in the production of 120 000 m^3 of bioethanol.
- The problem is the release of lipids from the solid part of the stillage. In addition to elevated temperatures may be used for special additives.

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Probable evolution

- Most likely corn oil extraction technology will be applicable and to improve especially on large units in the U.S. where the EPA requires the use of "Advanced Technologies", in which extraction of corn oil was included.
- EPA RFS2 requirement - must be applied to the total production.
- With improving technology and expanding aviation synthetic fuels technology will also spread to smaller production units and in Europe.
- 35 percent of U.S. ethanol plants implement corn oil extraction, adding
- The experts expects that number to double within a couple of years.

RFS2 – renewable fuel standard

Experiments

- Transesterification of corn germ oil
- Catalytic hydrotreatment corn germ oil

Parameter	unit	KO 1	KO 2
Density, 20°C	kg/m3	925	913
Kinematic viscosity, 40°C	mm^2/s	33,8	32,1
Iodine number	g I_2/100 g	124,6	120,4
Acid number	mg KOH/g	2,8	1,91
Content Na	mg/kg	0,8	0,9
Content K	mg/kg	84,6	88,2
Content Ca	mg/kg	4,26	5,8
Content Mg	mg/kg	44,2	47,6

Transesterification of corn oil

The preparation FAME from corn oil was standard procedure used alkali-catalyzed transesterification of oil with MeOH.

- Technology is a two-stage, with the first step after adding 78% KOH solution in MeOH, the resulting first-line G-phase done and then enters the second stage.
- Each step lasted 90 minutes, the temperature was 60°C.
- The proportion of catalyst is 0.8 wt%. to oil. The reaction mixture after a short period stirring vigorously for about 1 minute was left at a standstill.
- Final adjustment of the raw FAME to ensure all indicators EN 14 214:2011 consists of vacuum evaporation of unreacted MeOH, chilling of FAME, the filtration, the addition of 0.5% water, vigorous mixing, centrifugation, drying and antioxidant additives treatment (0.1% wt . *tert.* butylated hydroxytoluene).

FAME from corn oil – selected properties

Parameter	Unit	Method	FAME	FAME MD*	EN 14214
Ester content	% (m/m)	EN 14103	97	100	min.96,5
Density, 15°C	kg/m^3	EN ISO 3675	886	882,6	860–900
Viscosity, 40°C	mm^2s^{-1}	EN ISO 3104	4,466	4,062	3,5–5,0
Acid value	mg KOH/g	EN 14104	0,20	0,15	max. 0,5
Oxid. stability, 110°C	h	EN 14112	3/5,7*	2,7/6,2*	min. 6
Cetane number		EN ISO 5165	48,7	48,9	min. 51
Group I metals Na+K	ppm	EN 14109	0,39 +4,45	0,42 + 0,34	max. 5
Group II metals Ca+Mg	ppm	EN 14538	2,85 + 1,54	0,03 + 0,13	max. 5

**FAME MD – vacuum molecular distillation*

- Oxidation stability of FAME after finalization of the standard, set Rancimat test is relatively low
- Cetane number is relatively low and is influenced by double bonds in the molecule of methyl ester.

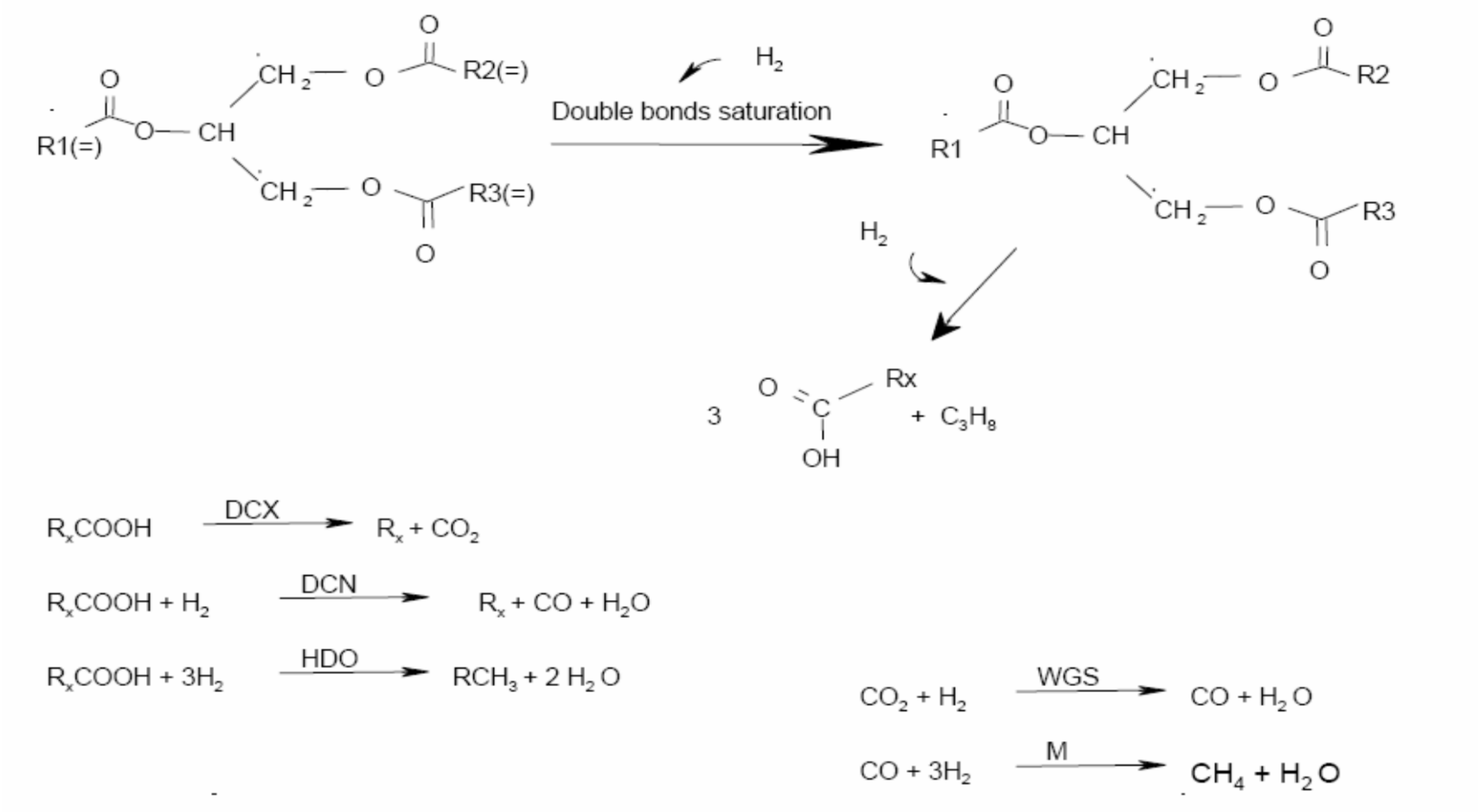
Second generation diesel fuels

- Direct conversion of TAG to liquid hydrocarbon fuels is a prospective technology of chemical industry.
- TAG present in vegetable oils and/or animal fats are transformed in the presence of hydrogen and hydrorefining NiMo, CoMo, NiW/γ-Al_2O_3 based catalysts are converted to hydrocarbons, mainly to n-alkanes at the temperatures above 300-360 °C and pressure at least 3 MPa leaving propane and CO_2 as side-products
- The mechanism of the reaction is complex and consists of series of consecutive steps, the fastest one being TAG transformation to fatty acids.

Hydrodeoxygenation of vegetable oils and fats

- One possibility to increase production of bio-jet and/or diesel fuel production via catalytic elimination of oxygen.
- As the catalyst can be used NiMo, NiW and CoMo catalysts in the sulfidic form.
- The advantage of the process is excellent emission profile of the product.
- Commercial processes: NExBTL, Ecofining, Axens.
- The catalyst offers Haldor Topsøe and Albemarle.

Hydrodeoxygenation- reaction ways



Stefano Melis et al.:, Catalytic Solution for the Co-Processing of Vegetable Oils in Conventional Hydrotreaters, 45th International Petroleum Conference, Bratislava, June 2011

Hydrodeoxygenation of corn oil

- Hydrodeoxygenation testing were carried out in a continuous flow tubular reactor, temperature range 360-380 deg. C, pressure 5,5 MPa, LHSV 1 h^{-1} and ratio hydrogen to feedstock form 500 to 1000 l / l. h
- The catalyst used in present study were three commercial catalysts (sulfidic form) in one reactor in series – $NiMo/Al_2O_3$, NiW/zeolite and WGS catalyst.
- Corn oil contains a high portion of unsaturated TAG which generates substantial reaction heat, dilution with 30% vol. of n-decane was used for regulation of reaction temperature.

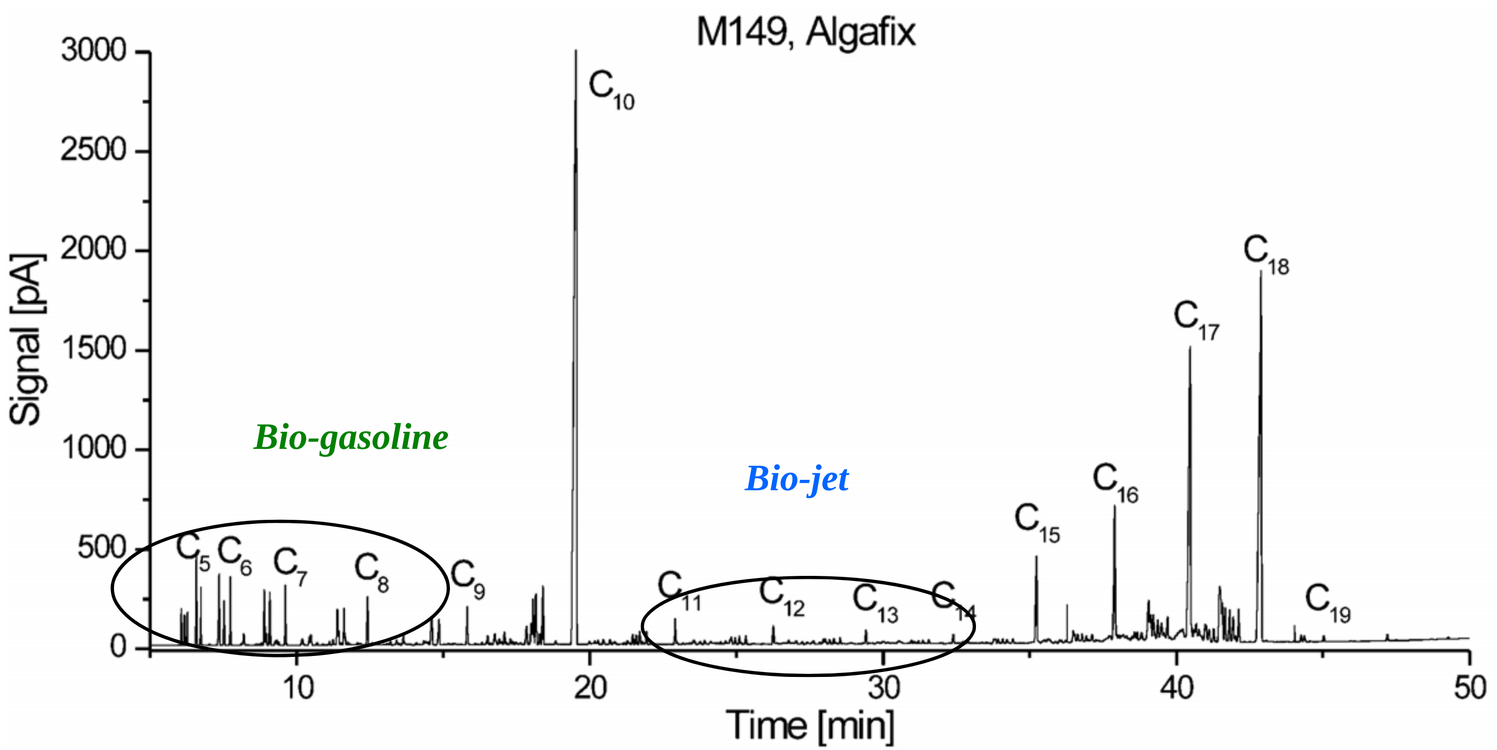
HDO of corn oil – results 1

Temperature, °C	380
Pressure, MPa	5,5
LHSV, h^{-1}	1
H2:HC l/l.h	540
Hydrocarbons C_1-C_5, % (m/m). of which:	4,81
CO	0,56
CO_2	1,97
Propane	1,79
Methane	0,16
Liquid product, % (m/m).	90,90
Reaction water, % (m/m).	4,81

- The content of n-alkanes in the liquid product was 59.99% (m/m) , the content of mono-methylated alkanes were 23.48% (m/m) and 15.28% (m/m) of unidentified alkanes.
- The reaction was highly exothermic, despite the dilution of n-decane.

- The reaction pathway involves hydrogenation of the C=C bonds of the corn oil followed by alkane production by three different pathways: mainly hydrodeoxygenation, decarboxylation and decarbonylation.
- Use of WGS catalyst had no significant effect on CO concentration.

HDO of corn oil – results 2



- Under the reaction conditions, the straight chain alkanes can undergo isomerization and partly cracking to produce isomerized alkanes with lighter alkanes.

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Summary -1

- Experimentally were tested two possible process technology of corn oil.
- The advantage of separating corn germ in the milling process is the possibility pressing of germ alone or with other feed. It is preferred particularly for processes of bioethanol and FAME in one location.
- Germ oil has qualitative properties suitable for the production of FAME and for process hydrodeoxygenation. Crude germ oil needs dewaxing and degumming.
- Extraction of corn oil from the whole stillage and DDGS with hexane is further possible oil recovery technology.

Summary - 2

- According to selected extraction technology it can be obtained from 1 to 2.5 %wt. corn oil on feed –corn.
- The extracted oil has a high acid number and requires modification of FAME production technology.
- Fatty acids in corn oil from extraction must be removed prior to transesterification. Highly unsaturated fatty acids chains result in a less stable biodiesel product since oxidation occurs at the double bonds when stored for extended periods of time.
- The use of a hydrocracking catalyst lead to products with a lower pour point, but with lower yields of liquid.
- The technology is suitable for production of bio-jet and renewable diesel fraction.
- Cetane number of diesel fraction is over 80.

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