State of the art technology for the production of advanced biofuels from lignocellulosic biomass, vegetable oils and animal fats.

Jozef Mikulec[1], Ján Cvengroš[2]

[1] VÚRUP, a. s., Bratislava, SR

[2] Faculty of Chemical and Food Technology, Slovak Technical University in Bratislava

The Second Bioeconomy Course University of South Bohemia
May 22, 2017, České Buděovice, Czech Republic

What is the bioeconomy?

- *„The bioeconomy comprises those parts of the economy that use renewable biological resources from land and sea – such as crops, forests, fish, animals and micro-organisms – to produce food, materials and energy."* [*https://ec.europa.eu/research/bioeconomy/index.cfm*](https://ec.europa.eu/research/bioeconomy/index.cfm)

Biofuel production technology can :

- *Generate* new jobs

  - in production of liquid biofuels 1,678 mil. work places

  - in the production of biogas - 382 thousand jobs

- Waste treatment and by-products treatments – i.e. in UK 16 mil tons/a, food and drink waste, processing residue, agricultural residues, crops, sewage sludge
- Reduce the carbon dioxide emissions
- Stabilize agricultural sector – increase income in rural areas

Liquid/gas biofuels in transport

- Transport biofuels typically refer to liquid and gaseous fuels produced from biomass and are commonly classified as conventional biofuels or advanced biofuels. There are a number of approaches to making this classification. They are based on feedstock, GHG emission savings, technology maturity, and product type and quality.
- Bio-ethanol is the most widespread bio-components which may be utilized alone, in a mixture with petrol or as a high octane component as an ether (Ethyl *tert*. Butyl ether). The principle of production is fermentation of sugar-yielding solutions that are derived from starch or sugar-yielding materials.
- Methyl esters of fatty acids (FAME) represent a liquid fuel from renewable sources for diesel engines either in pure form (B100), or more frequently as blends with fossil fuel (B5, B10, B30 etc.). FAME are prepared by catalysed transesterification of natural triacylglycerols (TAG) – plant oils and animal fats - with methanol.
- Biomethane from biogas.

Advanced bio-fuels - definitions

- Advanced biofuels are biofuels typically produced from non-food/feed feedstock such as woody biomass, wastes and residues (i.e. wood, wheat straw, municipal waste), non-food crops (i.e. grasses, miscanthus) or algae:
- Targeting similar or better end product properties than the biofuels currently on the market,
- Having low carbon dioxide emission or high GHG reduction[1],
- Demonstrating high sustainability (in accordance with the RED (2009/28/EC) and FQD (2009/30/EC) provisions).

EIBI (European Industrial Bioenergy Initiative)

In the US, the advanced fuels are limits to reduce greenhouse gas emissions, the process of evaluating the technology and the raw material is continuous.

Benefits of advanced biofuels

- creating thousands of new jobs,
- maintain and rural development,
- major contribution to energy security of the country,
- reduction of greenhouse gas emissions
- long-term sustainable alternative to fossil fuels

EIBI identified seven essential chains for the production of advanced biofuels. Six of them based on ligno-cellulosic raw materials, Seventh uses biomass produced in an aqueous medium. Basic technological processes are thermochemical (gasification, pyrolysis, torrefaction), biological (fermentation, the combination of biological and chemical processes) and microbial processes.

Worldwide production of biofuels

- Annual world production of bioethanol in 2015 was 98.3 million m^3. The highest bioethanol production in 2015 was -56.1 million m^3 in the USA, Brazil - 30 mil. m^3 and in the EU - 4.1 million m^3.
- The second most commonly used biofuels are higher fatty acid methyl esters. Their annual consumption in 2015 was 30.1 million. m^3, of which EU 11.5 million. m^3 Brazil 3,9 mil. m^3 and US 4.8 million. m^3. For the production of renewable fuel components for diesel engines were used triglycerides and free fatty acids contained in different kinds of oilseeds and animal fats.
- On the third place in production and consumption of bio-components got hydroge-nation product hydrodecarboxylation of TAG. Its annual production in 2015 was 4.9 million m^3, EU 2.5 mil. m^3 and USA 1.2 mil. m^3.
- Production of biogas in the world (2013) – 35,9 PJ, EU – 2,8 PJ

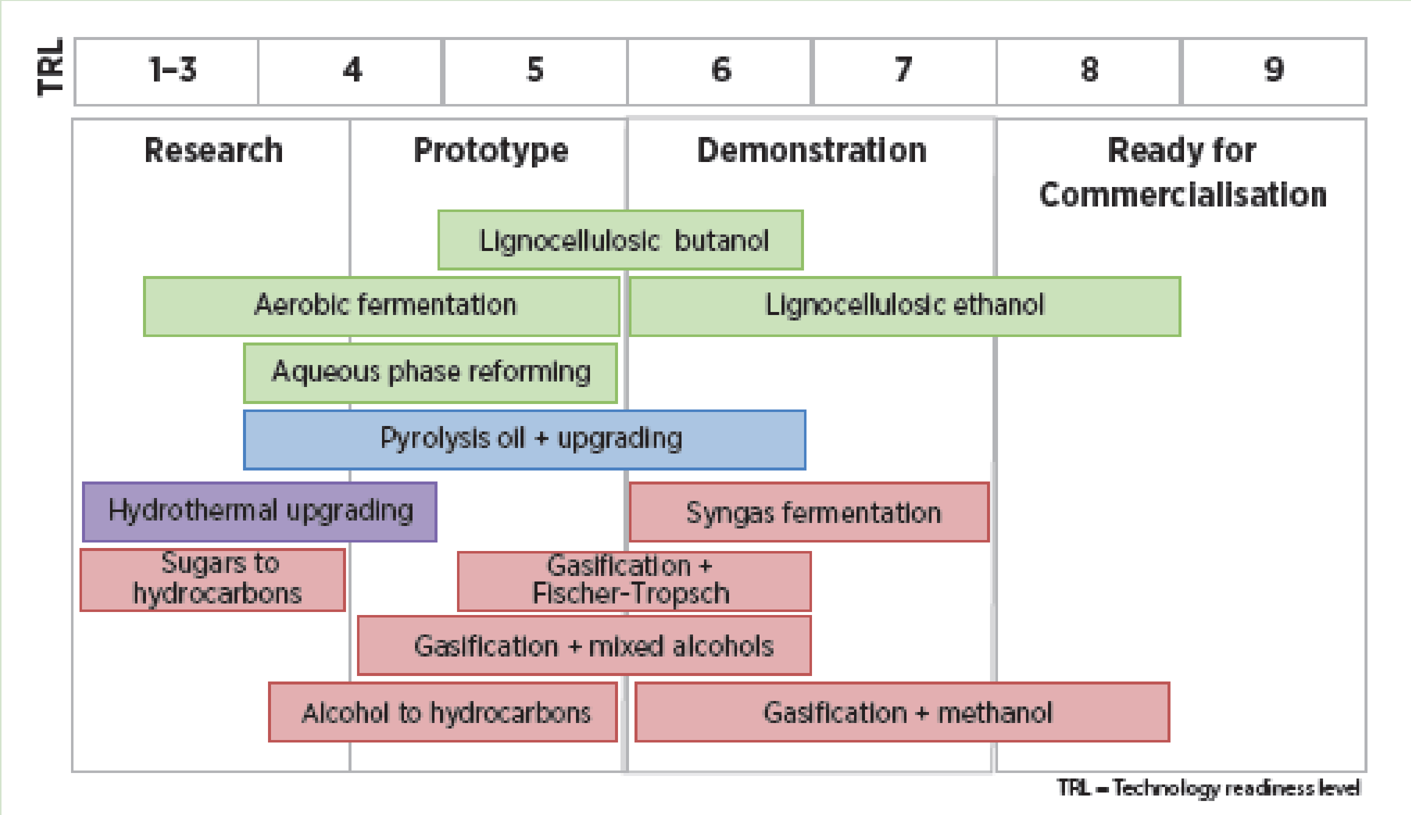
EIBI definition

- Demonstration plants are considered the last non-economic step to demonstrate the performance and reliability of all critical steps in a value chain so that the first-of-a-kind, commercial-scale industrial unit can be designed and performance guaranteed from the outcome of the demo unit.
- Flagship plants are the first-of-a-kind, commercial-scale industrial units of new value chains operating at an economically viable scale.
- Techno-Economic, Environmental and Social Evaluation Criteria: (Economic performance of the commercial concept, Future market deployment of the concept, Future contribution to reduce GHG emissions, Sustainably managed raw material, Environmental impacts other than GHG, Cost of avoided CO_2 equivalent, Energy efficiency to primary energy products, Societal impacts (Employment, labour and work conditions))

Boosting the Contribution of Bioenergy to the EU Climate and Energy ambitions

EIBI Implementation Plan 2013 – 2017, version 2014

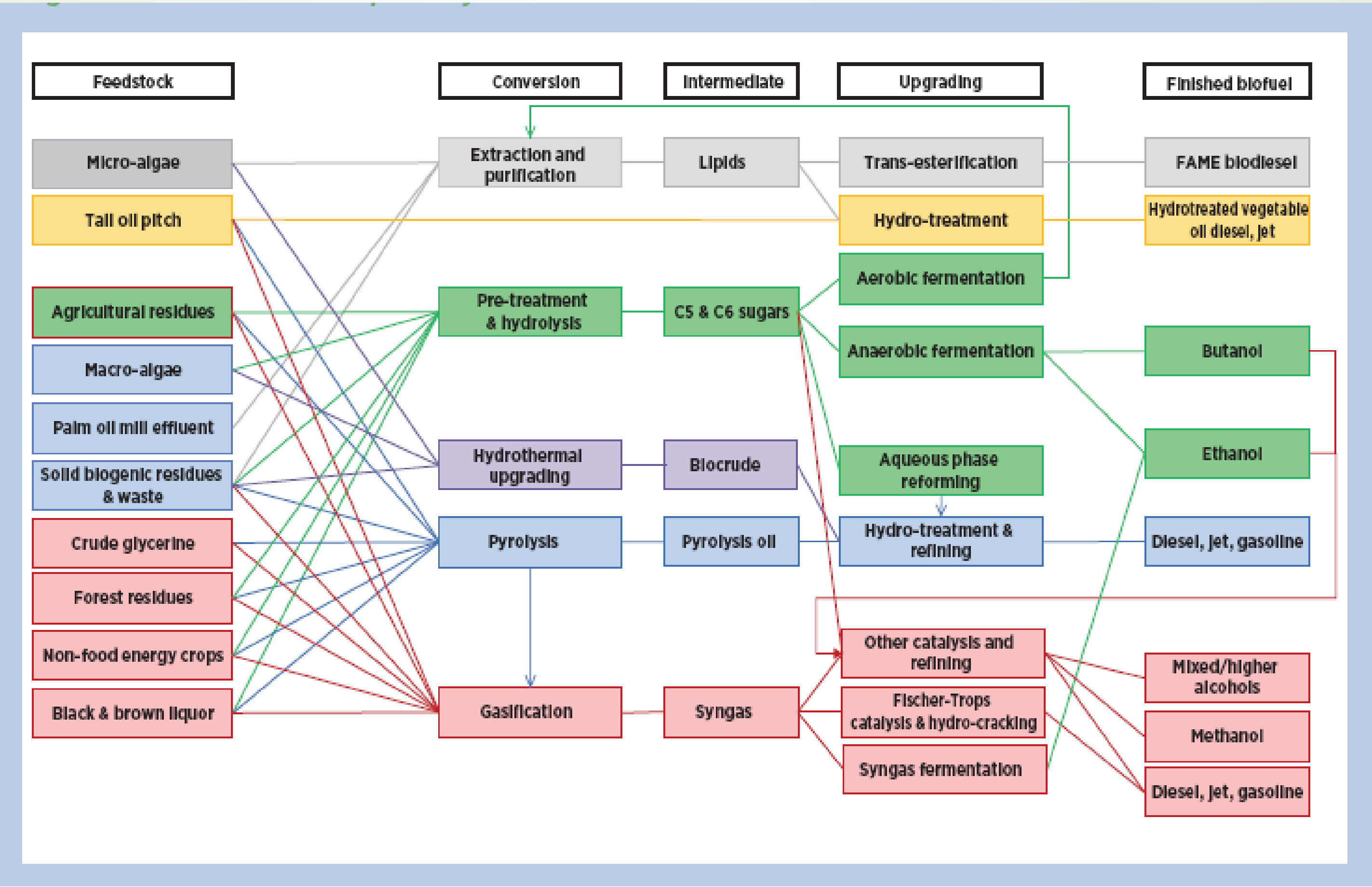
Commercial status of selected technologies



Note: Colours represent the principal conversion process, hydrolysis (green), pyrolysis (blue), hydrothermal upgrading (purple) and gasification (red).

www.irena.org/Publications *Advanced liqiud biofuels, 2016*

Advanced biofuels pathways

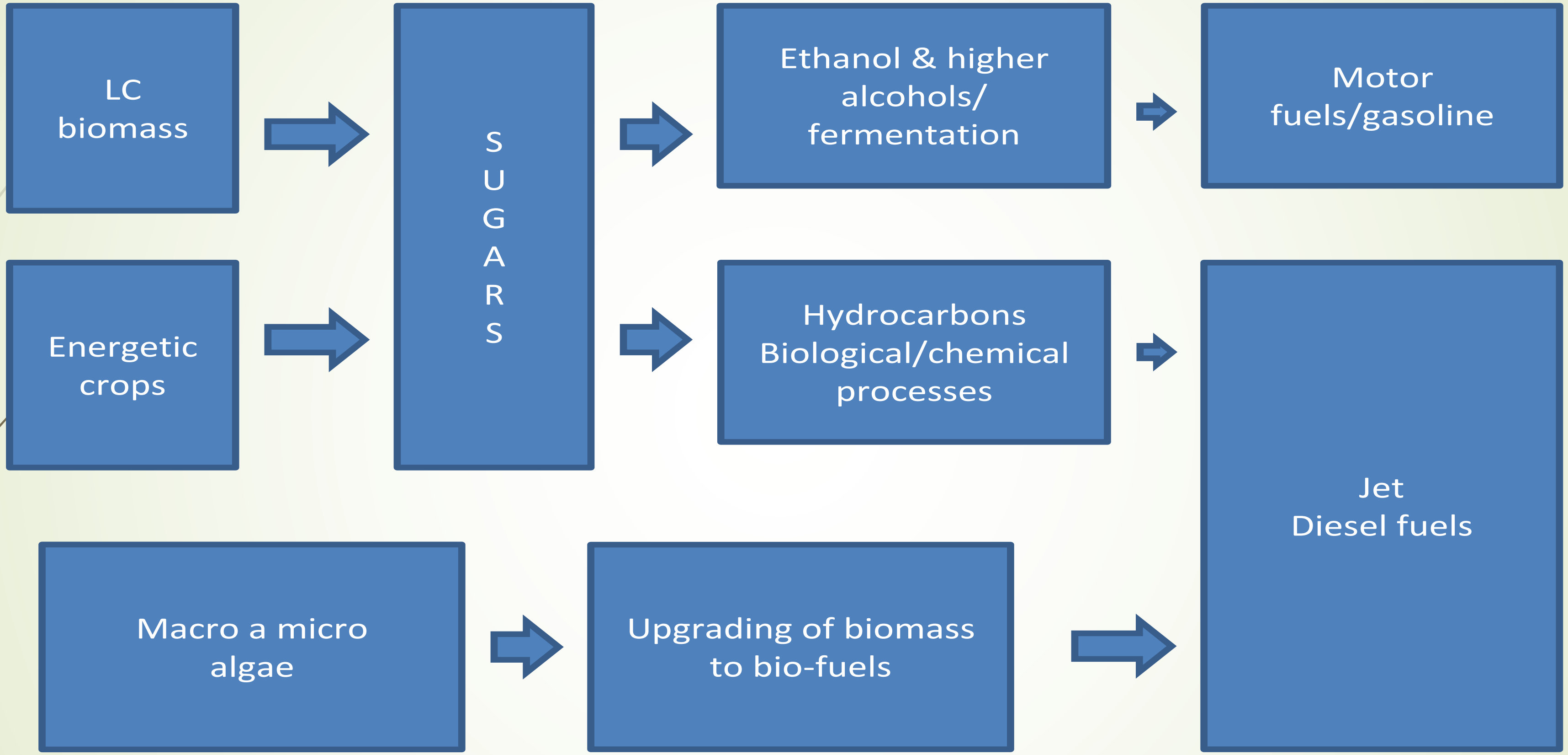


Note: Colours represent the principal conversion processes.

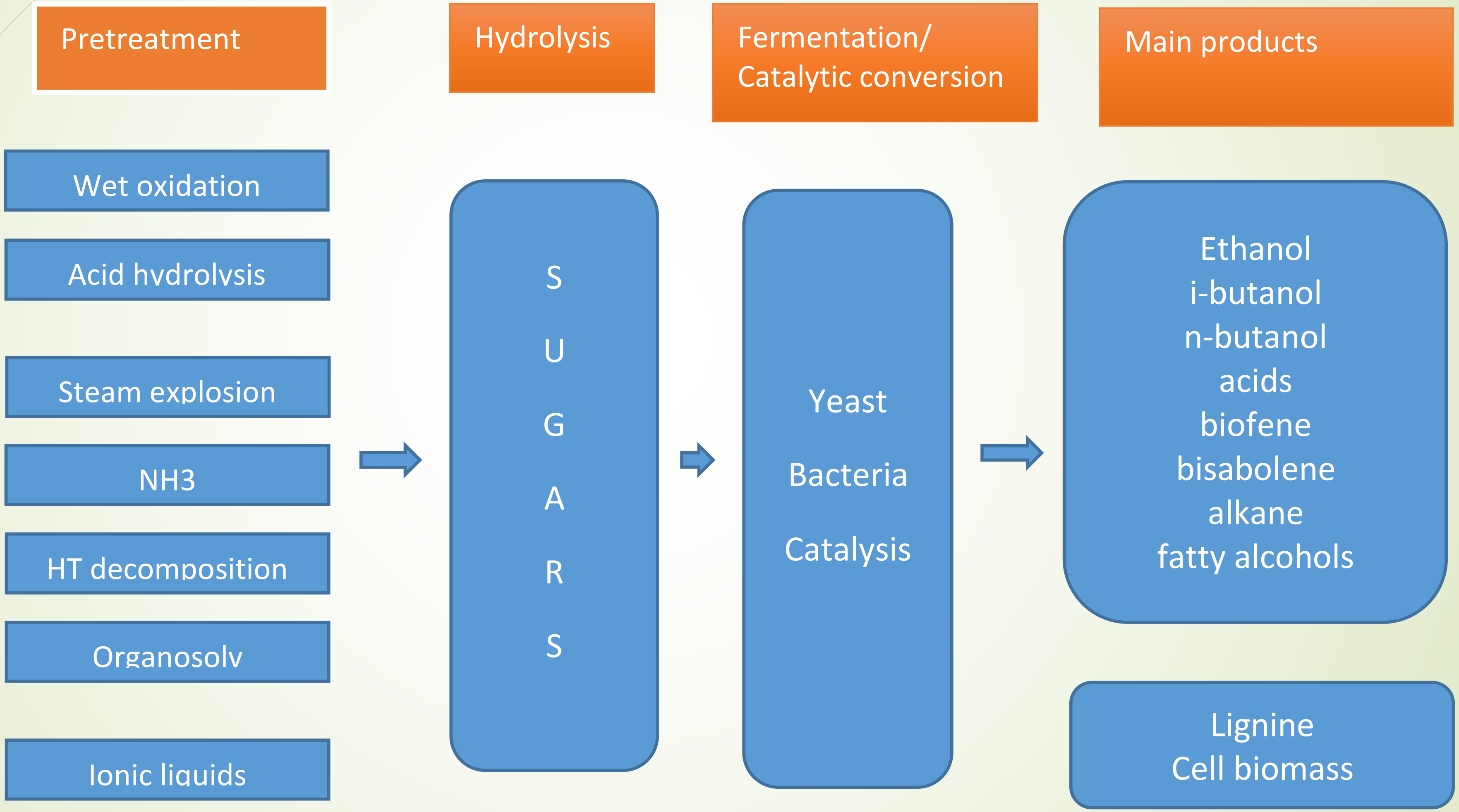
www.irena.org/Publications Advanced liqiud biofuels, 2016

Biocomponent	Specific bio-fuel	Biomass-feed	Technological process proces
Bioethanol	LC ethanol	Ligno-celulosic	**Enzymatic hydrolysis and fermentation**
Syntetic biocomponent	Synthetic hydrocarbons (BTL, FT)	Ligno-celulosic	**Gasification and synthesis**
	Biomethanol		
	Higher alcohols		
	Dimetylether		
	Ethanol & methyltetrahydrofurane		
Green diesel	Synthetic diesel (NExBTL, H-Bio) Synthetic diesel from cracking	Vegatable oils & fats Ligno-celulosic	**Hydrodeoxygenatio n** **Catalytic cracking**
Methane	Synthetic natural gas	Ligno-cellulosic Algae	**Gasification and synthesis**
Biohydrogen	**Hydrogen**	**Ligno-cellulosic** **Algae**	**Gasification and synthesis** **Biological processes**

EIBI value chain for advanced fuels



Biochemical processes



Production of ethanol from raw LC

- Logistic support of quality raw materials throughout the year is one of the key parameters for commercial production, which affects the subsequent conversion process, and sets the price of the final product.
- Initial expectations showed that LC resource base is relatively inexpensive and the development of conversion technologies will be quick.
- The reality is different, the raw material base is more expensive raw materials require pretreatment and separation of contaminants and also its processing technology was developed late.
- The content of ethanol is lower, the problem of fermentation inhibitors (furans) resulting from the hydrolysis of the sugars.
- In terms of technology, biochemical processes have greater potential for cost reduction in comparison with the thermo-chemical processes.

Bioethanol from LC in USA and Kanada

	USA	Canada
Total production units of bioethanol from raw LC / capacity mil. L	15/380	4/178
Number of expected new production units/ capacity mil. L	9/814	2/443

Source: *Ethanol Producer Magazine January 2016*

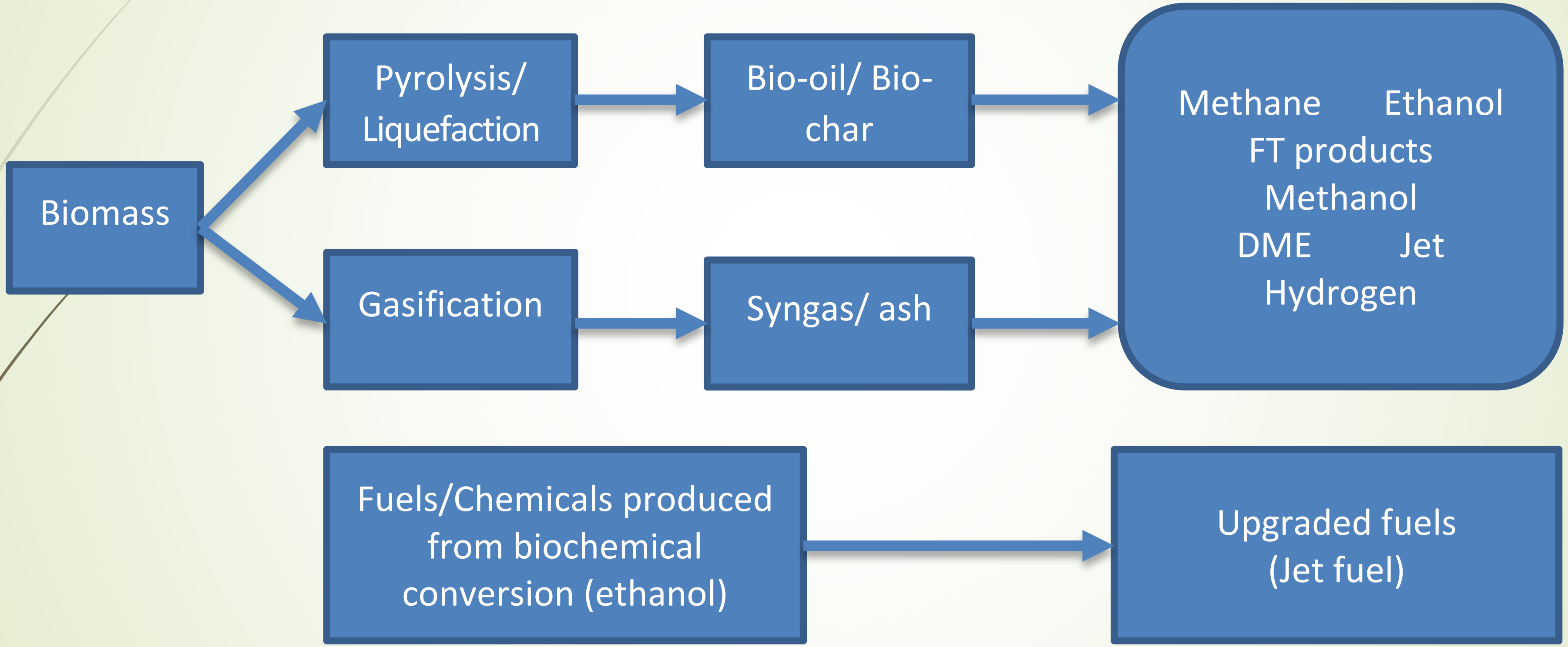
Bioethanol realised technology_1

Investor	Locality	Capacity	Capex	Feedstock	Technology
Beta Renewables	PROESA™ Crescentino,I	40kT ethanol 13MW heat	150 mil. euro	Rice straw bagasse	Steam explosion, enzyme
POET DSM	Project Liberty Scotland, SD	76 mil. L ethanol, biogas	275 mil. USD	Corn residue	Acid hydrolysis, enzyme
Abengoa Bioenergy Biomass of Kansas	Hugoton, Kansas	100 mil. L ethanol 18 MW energy	685 mil. USD	straw, agricultural residue	Thermochemical pretreatment, Enzymatic hydrolysis Fermentation enzyme &yeast
DuPont	Nevada, Iowa	114 mil. L ethanol	200 mil. USD	straw, agricultural residue	Ammonium, bacteria *Zymomonas mobilis*
Fiberight	Targeted Fuel Extraction Blairstown, Iowa	23 mil. L Ethanol, 17 mil. L biogas	25 mil. USD reconstruction	Municipal waste	Enzyme, fermentation with bacteria,

Bioethanol realised technology_2

Investor	Locality	Capacity	CAPEX	Feedstock	Technology
Inbicon a DONG Energy	Kalundborg, Dánsko	5,3 mil. L ethanol 11.1 kT C_5 sugars 14kT lignin biogas	Demo unit 54 mil. euro	straw	Hydrothermal pre-treatments Enzymatic hydrolysis
Granbio Cellulosic Ethanol plant,	Alagoas, Brazília PROESA™	83 mil. L/r etanol	190 mil. USD 75 mil. USD cogeneration	straw, bagasse	Steam explosion, enzyme
Clariant demo,	Sunliquid® Straubing, Nemecko		225 mil. euro	straw, agrocultural residue	Hydrothermal pre-treatment Enzymatic hydrolysis Fermentation C_5 a C_6 sugars

Thermochemical and hybrid processes



Partial oxidation of biomass

- The basis is the partial oxidation of the biomass to form the syngas comprising a mixture of CO and H_2.
- The process is exothermic, heat release can be used directly in technology and / or for renewable energy production.
- The condition for the further processing of the mixture, the adjustment ratio CO / H_2 and removing tar shares which are catalyst poisons in the subsequent phases of the technology.
- The synthesis gas may be used for the production of several types of biocomponents.
- Production of synthesis gas from fossil sources is a widely used process for the production of hydrogen respectively. synthetic hydrocarbons from coal or waste gas from oil production.

Biomass pyrolysis

- Bio oil from flash pyrolysis of lignocellulosic material is produced at atmospheric pressure at relatively low temperatures of 450-550°C at high heating rate of 10^3 to 10^4 K / s and a short residence time of about 1-3 s, after quenching r the short-chain cracking molecules are condensed.
- Fast pyrolysis of biomass as an effective conversion with high yield liquid product 70 to 80% with a high share of fuel input to be considered reasonable and promising technology.
- Compared to diesel fuel it contains a large amount of oxygenates (45-50% wt.), in particular esters, aldehydes, ketones, phenols, sugars, furans, terpenes, alcohols, and carboxylic acids. Many of the phenols in the form of oligomers of molecular weight 900 - 2500 g / mol. The composition depends on the input material - the biomass and the pyrolysis conditions (temperature, time, temperature profile).
- Demo Technologies: Bioliq technology, Empyro, Metso VTT, Biocrack BDI-OMV.

Synthetic bio-components - technology

Investor	Locality	Capacity	CAPEX	Feedstock	Technology
Solenafuels a British Airways	Rafinery at Coryngdon, UK	120kT fuels 40MW energy	?	Wastes500kT	Gasification with plasma associated with the use of the process of cleaning the syngas (Fluor), FT synthesis (Velocys) FT processing of products to fuels (UOP)
Chemrec	Pitea SE	Demo unit 4t/day Start in 2010	14 mil. euro	Wastes from cellulose production	Waste gasification and DME synthesis
Consortium *	BioTFuel, Rafinery Dunkerqu e, F	200kt/r	180 mil euro	LC wastes 1 mil. t	12MW pressurized gasification PRESFLO-PDQ (Uhde) followed FT synthesis to diesel and biojet

**Axens, the French Alternative Energies and Atomic Energy Commission (CEA), IFP Energies Nouvelles, Avril (ex-Sofiprotéol), ThyssenKrupp Industrial Solutions a Total*

HVO technology - principle

- The technology HVO used CoMo and NiMo sulphided catalysts of a modified form of the carrier, which is resistant to the reaction water that formed in the process.
- Similar catalysts are used for the desulfurization of petroleum fractions. The technology included three reactors, the first of the raw material removed impurities (Ca, Na, K, Mg, P), which act as catalyst poisons and could reduce the running time of the catalyst.
- In the second reactor at special catalyst (CoMo / carrier, NiMo / carrier) will transform triglycerides to hydrocarbons.
- Since the C_{17}-C_{18} hydrocarbons have a high pour point and that of the third reactor, where such hydroizomerization take place the branched hydrocarbons with low freezing point (Pt / zeolite, H).
- In the distillation column the product was fractionated by gasoline, diesel and aviation fuel.
- The technology contain also part the purification of hydrogen from the reaction products (water, CO_2, CO, propane).

Technologies HVO/HEFA_1

- At present, the production of HVO fuel is the third in volume of biofuel produced.
- Largest producer and owner of NExBTL technology is a Finnish oil company Neste, co-owner of the Finnish government, 50.1% of the shares.
- In the production 10 types of raw materials and 60% are waste and non-food raw materials (Jatropa, fish oil, animal waste fats) are used.
- HVO is an investment expensive technology. Currently commercial offers NExBTL process of Neste Oil, the process of UOP / Enichem Ecofinning ™ Vegan and fiction. Axens.
- The advantage of the location in the refinery is built up infrastructure in all areas.
- Revamp of desulphurization unit represents one third of the cost of a new unit ($ 40-10 / barrel). It is the best location with the possibility of shipping / river transport of raw materials.

Technologies HVO/HEFA_2

- At the same time the demand for green fuels has been developing demand for aviation fuel which can be produced in the same method.
- Interesting technologies were used in the processing of waste from pulp. The crude tall oil in Pitea is esterified with methanol using sulfuric acid (SunPine process). The resulting methyl ester is distilled off and after transport to the refinery Preem in Gotteburgu, SE is hydrodeoxygenated to the HVO fuels.
- Neste company announced in September 2015 a new investment in bio-refineries in Rotterdam, where it will be separated propane from of-gases as bio-LPG. The investment is worth 80 million. euro and will start operation in late 2016 with a capacity of 40 kt / y. Exclusive distributor of the company SHV Energy.
- In addition to stand-alone investment is operated more co-processing - refining gas oil in a mixture with a vegetable oil / animal fat with a capacity of 1326 mil. L

Technologies HVO/HEFA_3

- Investment costs for HVO operations depend on the capacities ; there are very high for low and very high capacity. Medium-sized manufacturing HVO have a capital cost of between $ 30-40000 / bpd.
- To compare the investment costs for oil processing is 15 to 20,000 € / bpd, for biodiesel is $ 20-30000 / bpd. Operating costs are similar, 80% of the cost is material.
- The price for HVO is favorable compared to FAME, in 2010 ranged from + 20 + 30 US ₵ / L (premiums for higher energy content, low temperature properties, brand value).

**Natural Resources Canada. Study of Hydrogenation Derived Renewable Diesel as a Renewable Fuel Option in North America. Final Report 2012.*

HVO/HEFA production units

Locality	Capacity	OPEX	Production	Feedstock	Technology	Operator
Realised						
Porvoo#1	190 kt/r	€100 M	2007	Oils & fat	NexBtl	Neste Oy
Porvoo#2	190 kt/r	>€100 M	2009	Oils & fat	NexBtl	Neste Oy
Singapur	800 kt/r	€550 M	2010	Palm oilj	NexBtl	Neste Oy
Rotterdam	800 kt/r	€670 M	2014	Palm oil	NexBtl	Neste Oy
Gotteburg	100 mil. L	€23 M	2013	Tall oil		Preem Refinery
Geismar, L, USA	284 mil. L	$150 M	2014	Waste fat	Bio-Synfining®	Renewable Energy Group
Lappeenranta, Físko	100 kt/r	€175 M	2015	Tall oil	UPM Research	UPM Bio Verno
Norco, LA, USA	0,5 mil. m^3/r	$368 M	2014	Waste oil, non-edible oil	UOP/ENI Ecofining™ Honeywell Green Diesel™	Darling International Inc. a Diamond Alternative Energy, LLC
Planned						
Venice conversion of HT unit in refinery	300 kt/r	€100M	2014	Palm oil, later waste oil&fat	UOP/ENI Ecofining™	Enichem
La Méde at Marseille	500 kt/r	€200M	2017	Different oils incl, waste	Axens Vegan	Total

Biomass digestion to biogas

- Biogas is a gas that is formed by anaerobic microorganisms. These microbes feed off carbohydrates and fats, producing methane and carbon dioxides as metabolic waste products. This gas can be harnessed by man as a source of sustainable energy.
- Biogas is considered to be a renewable fuel as it originates from organic material that has been created from atmospheric carbon by plants grown within recent growing seasons.

Benefits of anaerobic digestion and biogas

- Production of renewable power through combined heat and power cogeneration
- Disposal of problematic wastes
- Diversion of waste from landfill
- Production of a low-carbon fertiliser
- Avoidance of landfill gas escape and reduction in carbon emissions

Biogas to biomethane

- When biogas is purified or upgraded to natural gas quality , it can be used in the same manner as fossil gas for natural gas vehicles (NGV).
- The largest producers of biogas as vehicle fuel in 2016 were Germany, Sweden, Switzerland, the UK and the US. Internationally, an estimated 500 plants produce biogas and upgrade the gas to natural gas quality equalling about 50 Petajoule (PJ)/a.
- The main environmental advantage of biogas as a vehicle fuel is that it can substantially reduce greenhouse gas (GHG) emissions in the transport sector (typically between 60% and 80% compared to gasoline).
- many countries worldwide support biogas use as vehicle fuel with tax exemptions, investment subsidies or incentives for biogas injection into the natural gas grid.

Algal biofuels

- Algal biofuels may be produced from macro algae (seaweeds) and microalgae via a range of technologies.
- A number of projects and pilot plants are now identifying the best types of algae to use and the best production technologies.
- Algal biofuels have attracted great interest as they do not compete with food crops for land use, but the technology is not yet as mature as that for some other advanced biofuels.
- Basic components of microalgae are proteins, carbo-hydrates and lipids. Depending on the type of algae and condition of cultivation may contain up to 60% lipids.

Microalgae can produce various lipid compounds, which can be divided into two groups:

- polar phospholipids (phosphatidylinositol, phosphotidylcholine, phosphotidyletanolamine), sulpholipids, glycolipids as a combination of oligosaccharides and lipids,
- neutral triglycerides, diglycerides, monoglycerides, waxes, and the isoprenoid type of lipids (tocopherols, terpenes, quinones and carotenoids), least polar lipids, chlorophyll, hydrocarbons, sterols and ketones .

Products of microalgae extraction

- With a traditional extraction using organic solvent is obtained an extract that contains the solvent, residual water, debris, colouring agents and extracted lipid.
- After removal of the solids (filtration) and removal of the solvent from the filtrate were obtained lipids.
- The ideal technological process for extracting of lipids from algae must provide selective extraction of lipids, minimum extraction of non-lipid contaminants (proteins).
- Technology must be effective, time and energy efficient, the solvent must be relatively inexpensive and safe.
- Technology for utilization of carbo-hydrates are similar as other LC source.

Algae cultivation

- Open pond is cheaper alternative for mass production, problems with water evaporation, possible infection and collapse of system
- Closed PBR is able to produce high concentration of algae biomass with less risk of possible contamination (4-7 g/L) , less of water evaporations loss, higher investment
- Volumetric growth rate for tested algae strain was 1,1-2.8 g/L.day, total volume of PBR 107 000 m^3.
- For mid European climate is possible to use cca 210 days from April to end of October

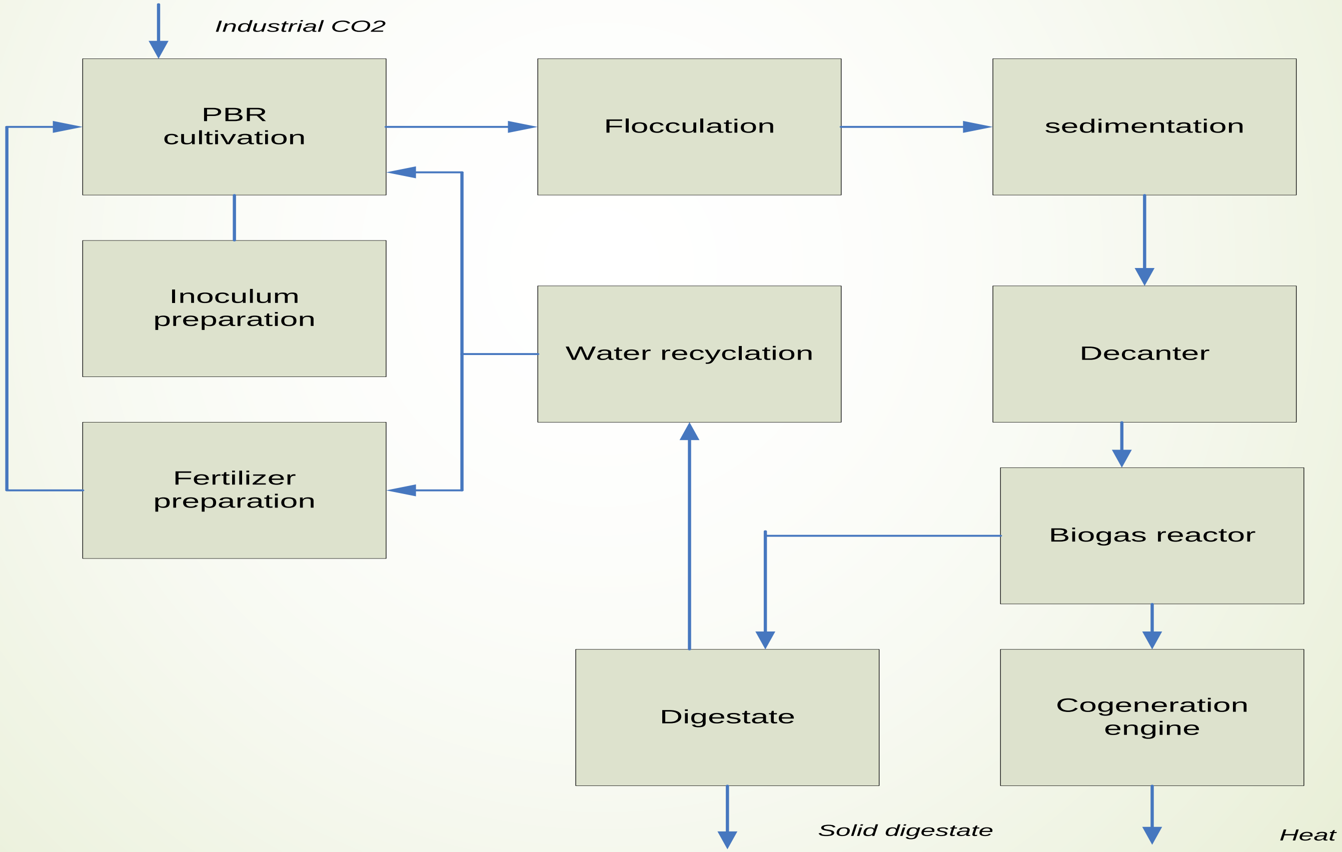
Harvesting

- The bottleneck of technology use of microalgae for fuel production is the cost of concentrating biomass. In the case of use of algal biomass for digestion or co-digestion is sufficient to concentrate to the 5-10% of dry matter.
- High molecular weight polyacrylamide polymer flocculants was effective for the tested microalgae. The tested polyacrylamide flocculants do not require pH adjustment like polyelectrolytes.
- The highest efficiencies were registered for the flocculants with higher cationicity, which removed more than 95 % of the cells of *Scenedesmus obliquus* and *Scenedesmus subspicatus*, *Synechoccocus nidulans* and *Parachlorella sorokini*ana, in the Log phase at concentration of 2 mg/L – 5 mg/L
- On the effectiveness of flocculation has a great influence presence and concentration of AOM.

Integration of microalgae with biogas plant

- The integration technology cultivation of algae using waste CO_2 and algae digestion process has a great environmental and economic dimension.
- For the production of bio-methane are more suitable algae which produce higher share of total lipids.
- A high concentration of nitrogen, during anaerobic digestion of protein-containing algae, have potential toxicity to methanogenic bacteria.
- The fatty acids in the lipids are highly influenced by the composition of growth medium
- Use of microalgae for renewable electricity and heat production is brings environmental benefits.
- Supply of nutrients for algae cultivation (N&P) is important for GHG emissions.
- Algae cultivation have high synergy potential with waste water –low fresh water consumption , decreasing additional nutrient input.
- Better option in terms in land use in comparison with other agro-products.
- We need new technology development and energy efficient cultivation, strain selection, processing of algae.

System coupling microalgae with biogas production



Anaerobic digestion

- Composition of the algal biomass is not beneficial for digestion to biogas because it contains disadvantageous C/N ratio in the range of 4-9, while the optimum ratio is in the range of 20-40. Co-digestion with classical feed and agricultural wastes are solution.
- Releasing higher concentration of ammonia in the digestion of protein is toxic to methanogenic bacteria.
- On the digestion of algae significantly affects their pretreatment, which accelerates the hydrolysis of the cellulose component in particular.
- We calculate with production of biogas 300m^3/T TVS.
- The advantage of algae digestion was the biogas composition, as the high concentrations up to 75-80% vol. methane were reached

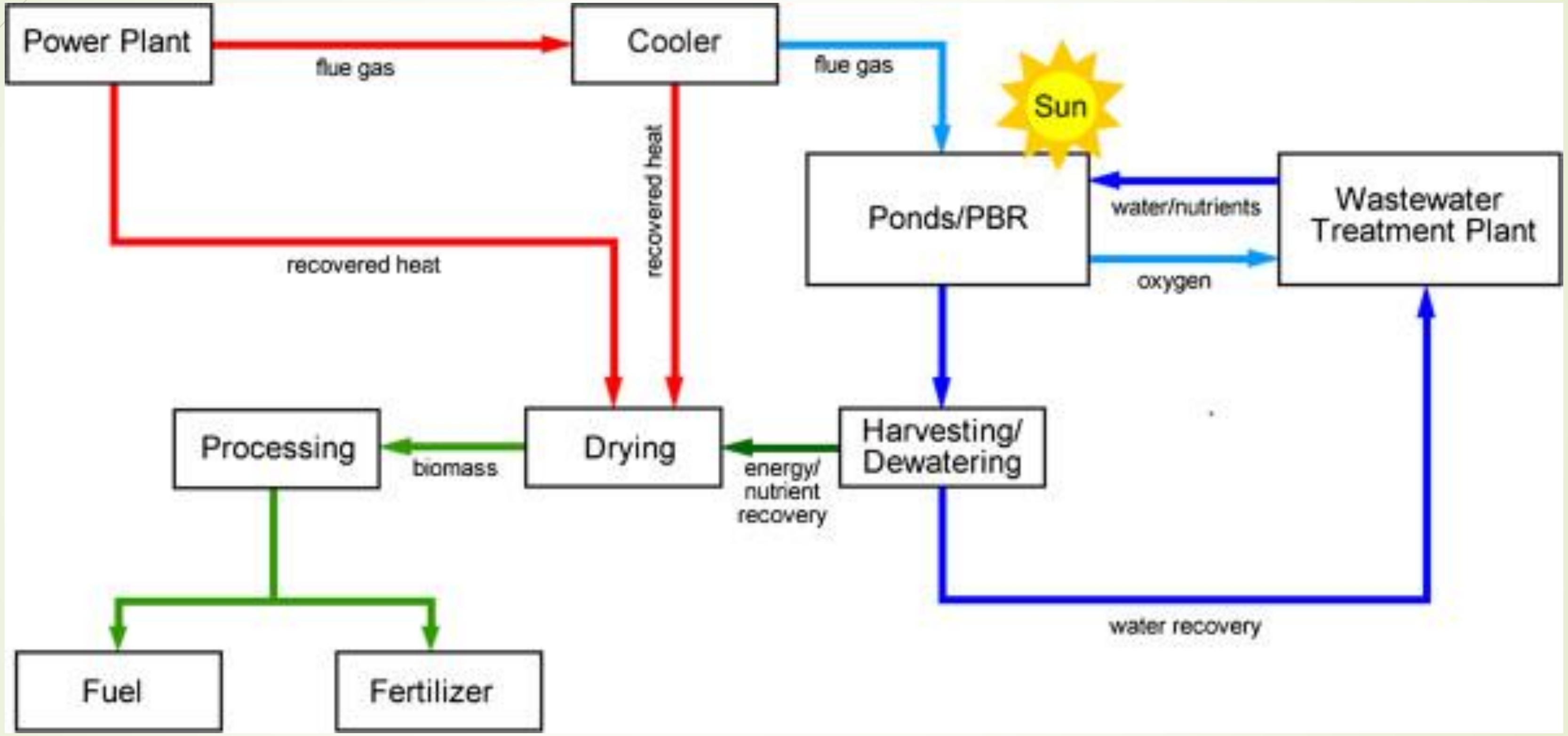
Recycling of digestate

- Anaerobic digestion of the algae leads to the production of digestate composed of organic and mineralized matter. During this step 60% of the carbon fraction of the algae is degraded.
- The solid fraction can be used as a soil conditioner, bringing fertilizers to the soil and increasing its organic content.
- The liquid part of the digestate with mineralised matter is reinjected in the mixing tank with addition part of minerals (mainly N, P, K) and is considered as fertilizers for the algae.
- Recycling will reduce size of the digestate tank because its size is designed for a period which should not be fertilized (180 days).

Additional aspect

- Location of microalgae cultivation will affect – productivity, evaporation in open pond.
- Artificial light – increasing productivity with using of renewable sources of energy (solar)
- Use alternative source of energy for cultivation and harvesting
- Very important is effective pre-treatment of algae biomass to increase yield of methane and higher organic loading rate (e.g. enzyme, thermal or catalytic hydrolysis). Pretreatments are used to increase the reaction speed and the total biodegradability of particulate matter,
- A higher concentration of microalgae in the input flow would increase the organic loading rate
- The choice of the algae strain could also lead to a significant improvement of the results of the LCA.
- Co-digestion with a substrate presenting a high carbon fraction, allows one to increase the global C/N and hence to reach a more favorable range for anaerobic digestion.

Integration of microalgae with WWT



Source: Aquat Biosyst. 2013; 9: 2.

Major risk of advanced fuels expanding

- Technical barriers

Non-technical barriers:

- The price of crude oil
- High production costs compared to fossil fuels
- Finance availability and supply chain risk
- Uncertainty about environmental performance
- Availability and price of feedstock
- Efficiency conversion technology and its price
- Development of infrastructure and logistic
- Uncertainty about social impacts

Acknowledgement

- This work was supported by the Agency for Research and Development under the contract no. APVV-0665-10 and APVV-0415-11.