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Outline:

- 1. Chemistry to agriculture
- 2. Chemurgy a turn from 1920s to present
- 3. RES a lesson learned
- 4. Conventional chemical platforms and derivatives
- 5. Polish example of lignocellulosic biorefinery (demonstration stage)
- 6. Polish example of sugar biorefinery (research stage)
- 7. Two sentences

Key points:

- 1. sustainable development needs sustainable industry
- 2. sustainable industry needs sustainable integration of agricultural and chemical industries

Chemistry to Agriculture – facts in brief

Nitrogen fixation (e.g. Desfosses, 1828; Kjeldahl method to analyze the amount of existing nitrogen present in organic compounds, 1956) Haber-Bosh process (production of ammonia at industrial level, 1913) Chemical fertilizers (granulated fertilizers 1930, suspension fertilizers 1965, time-release encapsulation at present) Green Revolution (hybrids, maximization of nitrogen uptake with chemical fertilizers, Mexico, wheat production 1943) Bordeaux method and fungicides (copper sulfate and hydrated lime (Bodeaux mixture) to combat mildew in vineyards, Pierre M. A. Millardet 1882, dithiocarbamate fungicides 1934, strobilurin fungicides 1996 DDT and pesticides (insecticide DDT, Paul Mueller, 1939) Farm mechanization (diesel-oil-powered tractors, Benjamin Holt, 1904) Livestock protection (vaccination against the anthrax-causing organism, Louis Pasteur 1881, anti-parasitic Ivermectin 1981) Saccharin and sweeteners (artificial sweetener Saccharin, John F. Quenny 1901) Vitamins and minerals (A (beta-carotene) – synthesized in 1947, C (hexuronic acid /ascorbic acid) – isolated in 1928, GMO ,golden rice' – provitamin A - 2001) Preservation and manufacturing advances (freeze-drying 1906, deep-freezing food 1920, precooking frozen foods 1939, concentrates from fluids 1946) Food safety and quality control (rapid test methods which enable the detection of microbial food contaminants and control of food-borne epidemics) Food packaging (saran polymer, Ralph Wiley, 1930s) Refrigerants and chlorofluorocarbons (Thomas Midgley, Charles Kettering, 1931) Microwave ovens (Percy L. Spencer, 1945) Clean water (chlorine-based disinfectants, 1910)

Social perception of chemistry: artificial, noxious, toxic, carcinogen

agricultural chemistry agricultural industry

chemical industry

vs. chemical agriculturevs. industrial agriculturevs. industrial chemistry



agribased chemical industry - chemurgy

a science on the industrial use of agricultural raw materials for chemicals

Chemistry makes an added value to agriculture

Agriculture makes an added value to chemistry

Chemurgy as a branch of applied chemistry emerged in 1920s and 1930s (USA)

• ... industry turn to farm products for its raw materials (Wheeler McMillen)

Acc. to chemurgists

- ... "the human stomach is inelastic, but the human demand for the products of manufacture is never satisfied"
- ...chemicals found in farm products could provide industry with needed raw materials
- ...growing of farm products to serve industry should replace the growing of edible crops as agriculture's primary objective

Principal goals of chemurgy

- to develop new, non-food uses of crops
- to develop new markets for farm commodities that were often found in surplus
- to find profitable uses for various agricultural wastes and residues

pragmatic (industrialists – seeking out new resources (e.g. Henry Ford)

Movements:

* utopian (isolated, self-sufficient chemurgic economy (e.g. William Hale)

Source:

Permeswaran P. 2010. Chemurgy: Using Science Innovatively to Save American Agriculture from Overproduction.

Finlay M.R. The Failure of Chemurgy in the Depression-Era South: The Case of Jesse F. Jackson and the Central of Georgia Railroad. The Georgia Historical Quarterly. Vol. 81, No. 1 (1997), pp. 78-102.



George Washington Carver (agricultural chemist)

- "Black Leonardo" (Time 1941)
- "One of the 100 most influential inventors of all time" (Britannica Educational Publishing, 2010)
 - Contribution to development of: Chemurgy, Plant Breeding/Genetics, Food Science/Nutrition, Plant Pathology, Soil Science, Bacteriology, Botany and Mycology, Ecology, Systematics
- Among the achievements:
 - 300 derivative products from peanuts: cheese, milk, coffee, flour, ink, dyes, plastics, wood stains, soap, linoleum, medicinal oils, cosmetics
 - 118 derivative products from sweet potatoes: flour, vinegar, molasses, rubber, ink, a synthetic rubber, postage stamp glue.

Source: Wikipedia

http://content.time.com/time/magazine/article/0.9171.801330.00.html

The 100 most influential inventors of all time / edited by Robert Curley. 2010. Britannica Educational Publishing

Chemurgy

- industrial use of biomass for chemicals
 - biomass: food (soya bean, corn, wheat), non-food (willow, cotton), co-products, byproducts and wastes (forest trimmings, tall oil, straw)
 - processes: from simple ones such as milling to the more advanced ones such as chemical and/or enzymatic hydrolysis

History (some facts on chemurgy activities)

1920s-1930s

- WW I was labeled the "chemists' war" (e.g. poison gases, high explosives, and other chemicals)
- <u>macrolevel search</u> for simple agricultural substitutes for industrial raw materials
 - guayule rubber substitute
 - tung tree domestic substitute for paint and varnish oils
 - farm wastes vegetable alternatives to coal tar dye
 - soybean meal enamels for automobile paints, lubricants for casting molds, and numerous plastic car parts such as soybean-plastic trunk lid (Ford) and cars (Ford – soybean, hemp; today: parts of Toyota from seaweed)
 - corncobs, pine waste, hemp, sweet potatoes for industrial utilization (Ford)
 - grain alkohol (bioethanol) e.g. applied in blend with gasoline "agrol" (by 1928 in the USA: 2000 filling stations)
 - sugar beets, Jerusalem artichokes, and other farm products as the raw material for butanol, acetone, and butyl alcohol
 - flax, hemp, rice as potential raw materials for furfural and glycerin
 - cellulose brushes, motion picture film

"Farming Must Become a Chemical Industry"

"Future farms would be transformed into "agricenters," vast complexes centered on chemical factories that bore little resemblance to the traditional farm"

Sources:

Clark J.P. 2010. Chemurgy. Kirk-Othmer Encyclopedia of Chemical Technology.

Finlay M.R. 2004. Old Efforts at New Uses: A Brief History of Chemurgy and the American Search for Biobased Materials. Journal of Industrial Ecology, 7(3–4): 33-46 Photos: Wikipedia, http://www.fastcompany.com/1183909/toyotas-seaweed-cars-take-green-design-whole-new-level





History (some facts on chemurgy activities)

1940s-1950s

- after WW II:
 - shortage of food
 - shortage of numerous industrial raw materials: rubber, starch, hemp, paint oil, jute, sisal, tanning agents, fish liver oils, coconut oils, palm oils, essential oils, and other materials
- <u>microlevel search</u> for valuable components within agricultural products
 - e.g. <u>soybean</u> from thinking that it is a component of animal feeds or a source of vegetable oil to specific sources of: lecithin, glycerin, alkyd resins, proteins, as well raw materials for plastics, adhesives, fire retardants, and ingredients in various prepared food products
- biobased chemical processing
 - developments in fermentation chemistry, which offered opportunities to utilize citric, lactic, gluconic, and other acids in processed foods and medicines
 - biofuels
 - pharmaceutical applications of biobased materials, such as the development of dextran, a blood plasma extender derived from microorganisms found in cane sugar
 - synthetic hormones from natural materials as regulators for plant growth
 - feeds laden with antibiotics to enhance animal growth
 - pesticides as the materials for increasing yields
- development of crude oil and coal-based products

1960s-1970s

- petrochemical products
- smaller and smaller interest in chemurgy up to disappearing completely

1979: energy crisis – short time interest, seeking out new biobased fuels

1980s-1990s

- development of coal and petroleum based chemicals, globalization
- slowly growing support policy for biofuels
- no political incentives for development of other new biobased products



2000s: progress in development of renewable energy sources – bioenergy and biofuels (EU Directive (2008): 3x20 by 2020)



The Economist (June 28th 2008): Due to:

- advances in bioengineering
- environmental worries
- high oil prices
- new ways to improve the performance of oil-based products using biotechnology

a revival of interest in:

• using agricultural feedstocks to make plastics, paints, textile fibers and other industrial products that now come from oil



What we have learned from the technological progress in biobased energy generation?

- to discover new processes (or "old" processes anew) of chemical conversions of biomass to useful energy
 - to show that there is a great amount of organic wastes which may be converted to useful energy
 - to show that the biomass-based energy products present only a marginal potential in the biomass use rationalization

The opening for biobased economy – bioeconomy

• the new opening for close association of agriculture and chemistry – chemurgy



Interaction of the bioeconomy system

The EU vision of biobased industry by 2020

- share of biomass based chemical processes will increase to 25% (2% in 2005)
- growth rate for market of bioproducts 5.3% yearly
- the whole value added chain of biobased chemicals: >200 bn EUR
- new market associated only with biobased chemical industry: 40 bn EUR and 90,000 jobs

and in agriculture:

 75 bln L of bioethanol at the competitive costs, and as a result: ca. 15 bln EUR of extra income in the sector of agriculture



Conventional agrifeedstocks, chemical processes and products

Source:

Golden, J.S., Handfield, R.B., Daystar, J. and, T.E. McConnell (2015). An Economic Impact Analysis of the U.S. Biobased Products Industry: A Report to the Congress of the United States of America. A Joint Publication of the Duke Center for Sustainability & Commerce and the Supply Chain Resource Cooperative at North Carolina State University.

Source: Dammer, L., Carus, M., Raschka, A., Scholz, L. (2013): Market Developments of and Opportunities for bio-based products and chemicals.

Process flow of biobased chemicals

FIRST GENERATION

Corn Sugar Cane/Sugar Beet Soy & Palm Oils Cassava

FEEDSTOCKS

SECOND GENERATION

Switchgrass Jatropha Grasses Forestry (Hemicellulose & Lignin) Miscanthus

Glucose, Fructose, Xylo	ose, Arabinose, Lactose, Su	crose, Starch;				i	Syn Gas
C2 Route Ethanol to Ethylene Ethyl Acetate Glycol Acid Ethylene Glycol Acetic Acid	C3 Route Glycerol Lactic Proplonic Acid Malonic Acid Serine	C4 Route Succinic Acid Fumaric Acid Malic Acid Aspartic Acid Acetoin Threoine 3-Hydroxy-butyroad	ctone	C5 Rou Itaconic / Furfura Levulinic Glutamic Xylonic / Arabite	ute C6 Acid Cit al Sc Acid Ly Acid Glum Acid Gluc ol	Route ric Acid orbitol ystine onic Acid aric Acid	Syngas Route H2 Methanol Mixed Alcohols Oxo/Iso Synthes Products Fischer-Tropsch Liquids
			INTERMED	IATES			
Butanediol (BDO)	Succinic Acid	Butanol	Butadiene	Isoprene	Propanediol (PDO)	Acrylic Acid	Furans
C4 Molecules PBS PBT	C4 Molecules PBS PBT Solvents Deicing	Solvents Paints Butyl rubber PET Fuels	Rubber ABS	Rubber	Fibers Cosmetics Polyurethanes PBT	Coatings Adhesives Plastics	Polyesters Polyurethane Fuels
	Adipic Acid				Teraj	ohtalic Acid	
Nylons Resins Polvurethanes				PET Plasticizers			

J.S. Golden Duke 2015

Carolina State University.

Source: Golden, J.S., Handfield, R.B., Daystar, J. and, T.E. McConnell (2015). An Economic Impact Analysis of the U.S. Biobased Products Industry: A Report to the Congress of the United States of America. A Joint Publication of the Duke Center for Sustainability & Commerce and the Supply Chain Resource Cooperative at North (Bio)industry will be shaped by development of (bio)refinery and (bio)refinery processes



The value added biobased chemical processing



"nano", functional value of modified molecular structure (e.g. pharmaceuticals, cosmetics)

"micro to nano", molecular value (e.g. chemical platforms, bioplastics, biopolymers)

"giga to micro", energy value (e.g. biofuels)

"tera to giga", mass value (e.g. combustion, heat and electricity generation)

Poland

- \checkmark the chemical and agricultural industries function independently
- ✓ chemical industry: petrochemicals, plastics, mineral fertilizers, and pharmacueticals and cosmetics
- ✓ biomass industry: food processing and to a lesser extent energy generation, no statistics for biomaterials and biochemicals



Structure of the contribution of the food and chemical industries to the value of production output sold in Poland (2014)



Strategic Program (funded by National Centre for Research and Development, partly by industry): Advanced Technologies for Energy Generation. Task 4. Elaboration of Integrated Technologies for the Production of Fuels and Energy from Waste Biomass



Sugar biorefinery: raw material is sugar beet

(i) high yielding

(ii) relatively low sensitivity to climate conditions, and

(iii) a potential to be cultivated in relatively broad spectra of soil types

(iv) the area of cultivation dedicated to supplying sugar beets to sugar biorefineries has a potential to be significantly extended

(v) properties of raw material which make biorefinery processes comparable to those from sugar cane feedstock



Comparison of the chemical composition of sugar cane and sugar beet (dry matter is divided into sugars, soluble and insoluble compounds)

- ✓ WF in sugar beet cultivation is 935 m³/t; sugar cane: 1500 m³/t
- $\checkmark\,$ WF in production of ethanol from sugar beet is 355 L/L; sugar cane: 2885 L/L





Feedstock: whole sugar beet Pretreatment: Betaprocess





Sugar platform biorefinery

Feedstock: whole sugar beet



The bio-ethanol demo plant in Lelystad (NL)

Betaprocess: demo plant (NL)

Demo plant: microalgae cultivation (PL)

Adapted facilities

The transition of industry from linear to circular one



Instead of conclusions

More with less

The future belongs to those who understand that doing more with less is compassionate, prosperous and enduring, and thus more intelligent, even competitive.

Paul Hawken

Ephemeralization

... the ability of technological advances to do "more and more with less and less until eventually you can do everything with nothing".

Richard Buckminster Fuller



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e.g. soybean – variety of products

Human Consumption	Animal Consumption	Industrial Uses
Baby Food Soups Whipped Toppings Cookies Mayonnaise Peanut Butter Margarine High Fiber Breads Cheese	Bee Food Pet Foods Milk Replacers for young animals Cattle Feed Dairy Feeds	Candles Hair Care Products Lubricants Putty Alternative Fuels Ink Paper Coating Cosmetics Hand Cleaners
Beer and Ale Salad Dressings Antioxidants		Soap/Shampoo Detergent Crayons

