

THERMO CHEMICAL ENERGY PROCESSES

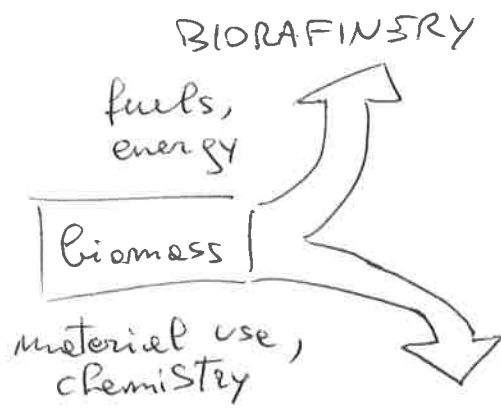
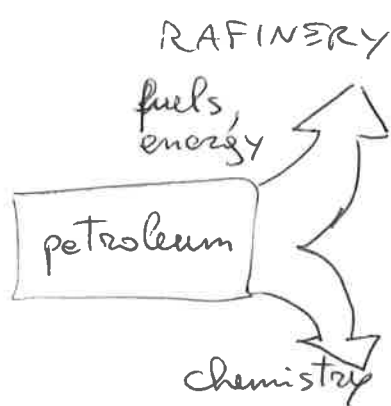
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① INTRODUCTION - HISTORY

The main time evolution was ~~by~~ from 150 years ago with coal-based chemistry to 50 years ago with petroleum based chemistry. The biorefinery is proposed as an alternative to the refinery; with similarities, such as product to obtain, process and equipment, and differences, such as the raw material to be processed. There was an evolution of products: ~~at 1801~~ ~~Poland~~

- Poland 1801, first biorefinery for sugar production from sugar beet;
- Germany 1812, starch hydrolysis to give sugar;
- Sweden 1835, starch enzymatic hydrolysis to give sugar;
- USA 1863, patent for the treatment of wood with basic solutions to obtain cellulose and pulp;
- Germany 1801, wood saccharification.



The fundamental of Biorefinery is providing code-defined basic substances for development of relevant industrial product family trees, usually containing biomass with preference for carbohydrates.

It is important to define constituents at molecular level, such as in photosynthesis reaction, with each organic matter and ashes:



Typically it is represented by proximate analysis and high heating values, which define organic matter (volatile and fixed carbon), moisture, ash and internal energy of combustion.

BIOMASS

Besides these ~~analysis~~ analysis, there is the ultimate analysis for constituents ratios of biomass, such as carbon, oxygen, hydrogen and others. We have different composition for different methods: dry, AR, maf.

Ash content expressed in weight (%) on dry basis and on as received material. Through the water content the ash contents ~~is~~ are related:

$$\% \text{ASH (dry)} = \% \text{ASH (AR)} * \frac{100}{100 - \text{water } \%}$$

Water content in weight (%), on wet basis (as received, AR). It is important to note that there can be a large difference between the water content of the material as it is available and the water content at the moment of analysis. Also by natural drying during storage the water content can be lowered.

The amount of volatile material is determined by standardized methods ~~the amount~~ It is expressed in weight % dry material, as received material or dry and ash free material.

The amount of fixed carbon is calculated as the remaining part as determined by the above mentioned standardized method according to the formulas:

DRY	F.C. = 100 - ASH (dry) - volatiles (dry)	(dried)
DAF	F.C. = 100 - volatiles (daf)	(no ashes)
AR	F.C. = 100 - ASH(ar) - water - volatiles(ar)	(undried)

② Proximate analysis carried out using a Thermogravimetric Analyser TGA 701. Typically, 200-300mg of solid samples were used to evaluate composition in terms of moisture content, volatile fraction, fixed carbon and ashes. The thermal program was as:

- 20°C/min ramp to 105°C in air; hold until weight constant ($\pm 0,05\%$) for moisture calculation;
- 50°C/min ramp to 800°C, hold time 7 min, in N_2 to determine volatiles;
- isothermal hold at 800°C in a ~~reactive~~ reactive environment (air) to determine the ashes.

In ultimate analysis it uses the formulas:

DRY	$C + H + O + N + S + Cl + F + Br + ash = 100$	(dried)
DAF	$C + H + O + N + S + Cl + F + Br = 100$	(no ashes)
AR	$C + H + O + N + S + Cl + F + Br + ash + water = 100$	(undried)

In many cases the oxygen content is not measured but calculated as the difference between 100 and the measured components.

The calorific value is expressed as High Heating Value and Lower Heating Value. The difference is caused by the heat of evaporation of the water formed from the hydrogen in the material and the moisture; the determination of the calorific value normally results in a value for the HHV. For comparison, HHV is also calculated from the elemental composition using the Milne formula (in $\frac{MJ}{kg}$):

$$HHV = 0,391 \cdot C + 1,322 \cdot H - 0,12 \cdot O - 0,12 N + 0,0686 \cdot S - 0,0153 \cdot Ash$$

A large number of data on the ash composition after conversion is available. In general these data are

expressed as weight % of oxides.

The metal content is expressed in $\frac{mg}{kg}$ dry material.

For each element it ~~is~~ ^{is} shown whether it is measured or the value is below the detection limit.

The biochemical composition of materials is expressed in weight % of the dry matter.

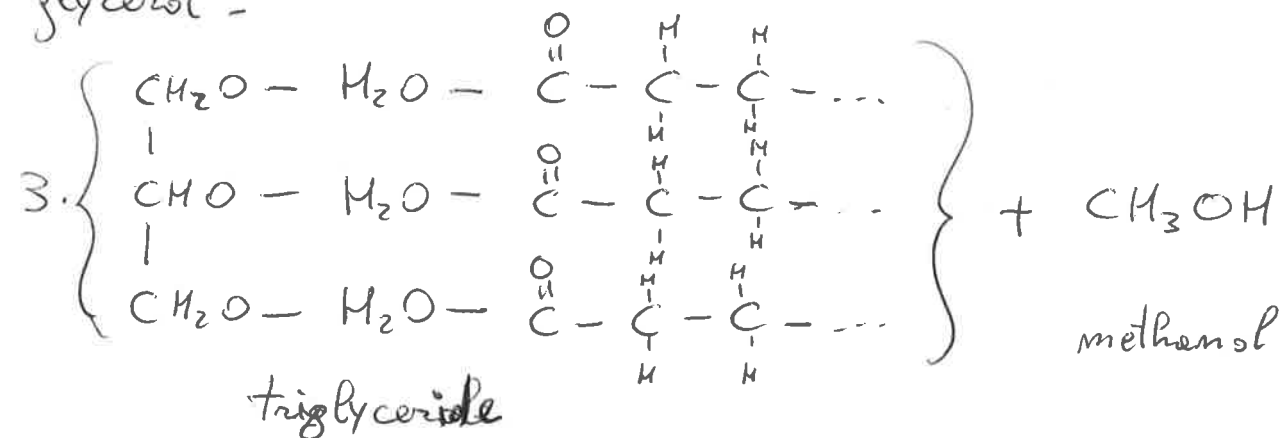
There are many kinds of biomass: solid-biomass could be from lignocellulosic, such as wood, with use agro-industrial, or also starchy crops, such as Italian agricultural and sugar crops or oilseed crops. Best production is about sugar cane, ~~is~~ composed by bagasse, barbojo and molasse. Other kinds of biomass could be from animals and solid municipal waste (MSW).

BIOFUELS

Biodiesel is the most important type of biofuel. Soybeans are used as a source of oil for biodiesel.

~~One~~ One of the biofuels is ethanol (C_2H_5OH) which born by sugar cane harvest $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 + \text{heat}$, so with an exothermal reaction, and HHV about of $28,7 \frac{MJ}{kg}$.

Biodiesel molecule is composed by ~~three~~ molecules of triglyceride and methanol, while a Triglyceride is made from the reaction between water, tree fatty acids and glycerol.



③ The standard enthalpy of formation (or standard heat of formation) of a compound is the change of enthalpy from the formation of one mole of the compound from its constituent elements, with all substances in their standard states (at 1 atm and 25°C). It is measured in units of energy per amount of substance ($\frac{\text{kJ}}{\text{mol}}$, $\frac{\text{cal}}{\text{mol}}$, $\frac{\text{kJ}}{\text{g}}$). All elements in standard states have a standard enthalpy of formation of zero, as there is no change involved in their formation. It is used in thermo-chemistry to find the standard enthalpy of reaction, this is done by subtracting the sum of the standard enthalpies of formation of the reactants from the sum of the standard enthalpies of formation of the products:

$$\Delta H_r^\circ = \sum (\nu \times \Delta H_f^\circ)_p - \sum (\nu \times \Delta H_f^\circ)_R$$

If the standard enthalpy of the products is less than the standard enthalpy of the reactants, ~~the~~ it will be negative. This implies that ~~the~~ the reaction is exothermic ($\Delta H_r^\circ < 0$). Conversely, the standard enthalpy of reaction will be positive for an endothermic reaction ($\Delta H_r^\circ > 0$).

Syngas, or synthesis gas, is a fuel gas mixture consisting primarily of hydrogen, carbon monoxide, and very often of carbon dioxide. The name comes from its use as intermediates in creating synthetic natural gas (SNG) and for producing ammonia or methanol. Syngas is also used as an intermediate in producing synthetic petroleum for use as a fuel or lubricant via ~~the~~ the Fischer-Tropsch process. Syngas is combustible and often used as a fuel of internal combustion engines. H_2 has less than half the energy density of natural gas. Production methods include steam reforming of natural gas or liquid hydrocarbons to produce hydrogen,

the gasification of coal, biomass, and it is also produced in some types of waste-to-energy gasification facilities.

methane steam reforming :

Fisher-Tropsch



Biogas typically refers to a mixture of gases produced by the breakdown of organic matter in the absence of oxygen. It mainly consists of CH_4 and CO_2 .

- CHARCOAL is a light black residue consisting of carbon, and any remaining ash, obtained by removing water and other volatile constituents from animal and vegetation substances. Charcoal is usually produced by slow pyrolysis, the heating of wood or other substances in the absence of oxygen.
- BIOCHAR is a name for charcoal when it is used for particular purposes, especially as a soil amendment. Like all charcoal, biochar is created by pyrolysis of biomass. ~~Biochar~~ Biochar is under ~~investigation~~ investigation as an approach to carbon dioxide emissions.

PHYSICAL BIOMASS CONVERSION

Dewatering is the removal of water from solid material by wet classification, centrifugation, filtration, or similar solid-liquid separation processes. It could have multiple-effect evaporator:

- common equipment to concentrate a solid-liquid stream from low concentration to high concentration;
- steam utility is optimized by adopting process intensification method.

Drying is a mass transfer process consisting of the removal of water or another solvent by evaporation from solid, semi-solid or liquid. To be considered "dried", the final

② product must be solid: long pieces, particles or powder. A source of heat and an agent to remove the vapor produced by the process are often involved. In bio-products the solvent to be removed is almost invariably water. In the most common case, a gas stream applies the heat by convection and carries away the vapor as humidity: air-drying. Other possibilities are vacuum drying, where heat is supplied by conduction or radiation, while the vapor so produced is removed by the vacuum system. Another indirect technique is drum drying, where a heated surface is used to provide the energy, and aspirators draw the vapor outside the drum.

Seasoning of freshly harvested trees by open-air drying requires long time periods to reduce the moisture level to about 25-35 ~~weight~~ weight%. Green wood chips can be air dried in less time. Continuous drying of wood chips, wood chunks, hog fuels with industrial dryers or in drying ducts installed prior to the conversion unit is an approach that is often used: rotary drum dryers. Thermo-chemical reactions can be designed so that incoming fresh ~~feed~~ feed is dried to the ~~desired~~ desired level by heat transfer from the hot reaction products. Size reduction often required before biomass is used as a fuel, it is used less ~~volume~~ storage volume with pneumatic transport. The physical dimensions ~~are~~ are accordingly to the final utilization and feedstock supply to the reactor.

• MEDIUM PRESSURE, PUSHING OR SUCTION

The pneumatic transport in phase diluted at medium pressures is based on the pressure or the depression generated by a blower inside one or more pipes. By means of an injection system, generally consisting of a tightened rotocell, the material is

introduced into the pipe, transported and conveyed to destination.

The advantages of pneumatic transport system in phase diluted are the simplicity of management and maintenance and the low costs of construction and consumption.

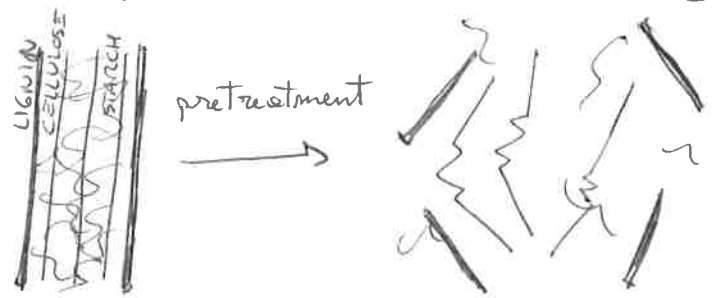
This transport is suitable for the transport of materials with a very low specific weight, such as granules, flakes, pellets, chips or powders.

The dense phase pneumatic conveying system consists of a propulsion tank and a transport line. The propulsion tank is filled with ~~the~~ the powder, granule, or pellet to be transported, after which it is pressurized from 1 to 6 bar; once the required pressure is reached, the discharge valve is opened and the product begins the path along the transport line.

During the transport phase, to avoid the formation of plugs of material along the pipes, the system, where necessary, provides for fluidization at the "pipe risky points". A fluidization system, positioned after the discharge of the propulsion tank, generates air jets that determine inside the pipeline intervals of air and material that allow the product to become fluid and therefore not to clog.

The advantages of dense phase pneumatic conveying are mainly evident over long distances. The pneumatic conveying systems ~~are~~ move the product at low speeds, preventing or reducing its degradation and limiting the abrasion of transport pipes, deviating valves and curves; it is therefore a great advantage for the handling of relatively delicate or abrasive materials. The transport speed increases proportionally with the advancing along the line, while the pressure decrease progressively

⑤ as the product approaches the end of the transport tube. The steam explosion is a hydrothermal treatment that makes it easier and less ~~the~~ severe from the environmental point of view the separation of three fractions constituting the common vegetable substrates. The process consists in the use of saturated steam at high pressure to rapidly heat the biomass in a continuous or discontinuous reactor. The material is kept at the ~~desired~~ desired temperature ($\approx 200^\circ\text{C}$) for a short period (10 minutes) during which the hemicellulose is hydrolyzed and made soluble, at the end of this time interval, the pressure is quickly restored to atmospheric pressure, resulting in an explosive decompression that further frays the biomass.



• MECHANICAL EXTRACTION

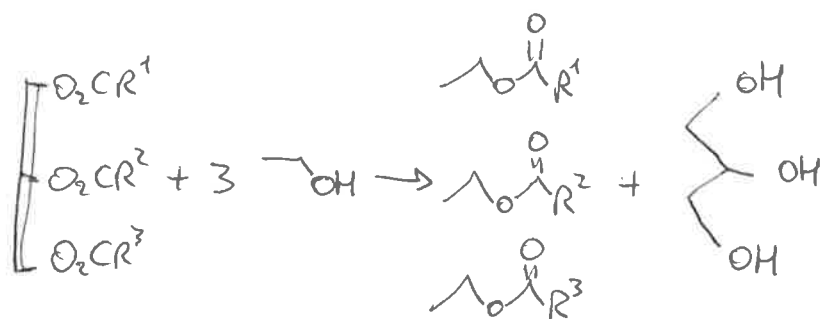
Oils can be extracted via mechanical extraction, by "crushing" or "pressing". This method is typically used to produce the more traditional oils, and it is preferred by most "health-food" customers. There are several different types of mechanical extraction. Expeller-pressing extraction is commonly ~~through~~ though the screw press, ram press, and Ghani are also used.

• SOLVENT EXTRACTION

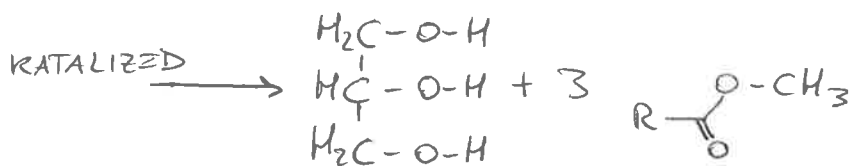
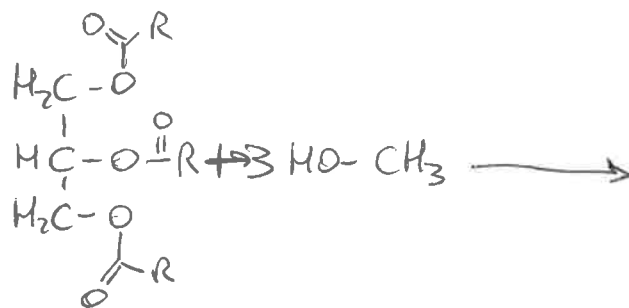
The extraction of vegetable oil in commercial application is commonly done by chemical extraction, using solvents, which produces higher yields and is quicker and less expensive. The most common solvent is petroleum-derived hexane. This technique is used for most of the "newer" industrial oils such as soybean and corn oils.

CHEMICAL BIOMASS CONVERSION

Triglycerides are reacted with methanol to give fatty acids methyl esters (FAME) and glycerol.



The reaction between the oil and the alcohol is a reversible reaction so excess alcohol must be added to ensure complete conversion.



Hydrolysis is a chemical conversion to have ethanol ~~from~~ from wood.

- CELLULOYSIS

The stages to produce ethanol using a biological approach are:

1. "pretreatment" phase, to make the lignocellulosic material such as wood or straw amenable to ~~hydrolysis~~ hydrolysis;
2. cellulose hydrolysis, to break down the molecules into sugar;
3. separation of the sugar solution from the residual ~~materials~~ materials, notably lignin;
4. microbial fermentation of the sugar solution;
5. distillation to produce roughly 85% pure alcohol;
6. dehydration by molecular sieves.

- THERMO-CHEMICAL APPROACH

Gasification, fermentation or catalytic reaction are using this approach to get syngas, ethanol and alcohols, respectively.

6) BIOCHEMICAL BIOMASS CONVERSION & ENG. TOOLS

Anaerobic digestion and fermentation are processes with biochemical conversion reactions. These kinds of conversion uses the ~~the~~ stoichiometry and reaction kinetics.

Stoichiometry network tells us how many and which components react ~~are~~ through the mass balance $\sum_i n_i M_i = \sum_i n_{i0} M_i$

The volume, (or mass), concentration is due to degree of advancement of reaction, $\sum_j \left[\frac{\text{kmol}}{\text{kg}} \right]$ for mass of the system and $\sum_j \left[\frac{\text{kmol}}{\text{m}^3} \right]$ for volume of the system.

$$\begin{cases} C_i = C_{i0} + \sum_j v_{ij} \xi_j \\ C_i = C_{i0} + \sum_j v_{ij} \epsilon_j \end{cases}$$

The degree of advancement of reaction is called reaction coordinate ~~rate~~ of reactants $x_A = \frac{n_{A0} - n_A}{n_{A0}}$

While we have n_{i0} known, n_i unknown and ξ_j unknown, in the expression $C_i = C_{i0} + \sum_j v_{ij} \xi_j$ there are ~~n~~ m freedom degrees and $n+m$ total unknown. So we need about $n-m$ equations of invariances.

The reaction rate r_i is the variation of concentration during the time $r_i = \frac{\partial C_i}{\partial t}$. In open systems chemically homogeneous and in steady state it's right: $r_i = \frac{q C_i - q_0 C_{i0}}{V}$

Instead, reaction kinetics describe the microscopic mechanisms by which the reactions actually occur and the correlation of the kinetics data by means of appropriate expressions of the reaction rate. ~~Am~~

Among the various elementary phenomena (steps or stages) that constitute the mechanism, some are purely physical, since they concern only the transport of reactants, products

and heat to the reaction point and vice versa, others are chemical, often with the formation of labile and little detectable chemical species. Some steps are fast, some slow, in the sense that they are characterized by large and small values of the rate coefficients, respectively. The slowest step determines the overall rate of the process. Expressions of chemical kinetics must be consistent with the laws of thermodynamic equilibrium.

• Kinetic constant is calculated $k = k_0 \exp\left(-\frac{E}{RT}\right)$

• Thermodynamic equilibrium is due to $K_c = \prod_i C_i^{\nu_i}$

So at equilibrium we have $\prod_i C_i^{\beta_i - \alpha_i} = \frac{k}{k'}$
(where β, k' of products and α, k of reactant)

- REACTION ORDER AND MOLECULARITY

The conventional molecularity represents the total number of moles of reactants that appear in the first member of the stoichiometric equation: similarly to the stoichiometric coefficients, it is therefore linked to the choices with which the stoichiometric equation is written. Strictly speaking, however, the molecularity expresses the mechanism of the microscopic chemical events: in this sense, it reflects the elementary steps and, correspondingly, the stoichiometric equation assumes a precise kinetic meaning. In this sense, the molecularity is always a small integer number, often one or two. For elementary steps, order and molecularity coincide, as well as the partial orders and stoichiometric coefficients match:

$$\beta_i = \nu_i \text{ products}$$

$$\alpha_i = -\nu_i \text{ reactants}$$

⑦ Conversely, for a reaction consisting of a sequence of elementary steps this is no longer true because the orders of the overall reaction are affected in some way by the real division in steps, while the conventional molecularity and the stoichiometric coefficients, referring only to the global stoichiometric equation, are disconnected from the network of the elementary events.

• CONVERSION
$$X_A = \frac{n_{0A} - n_A}{n_{0A}} = \frac{C_{A0} - C_A}{C_{A0}} = - \sum_j \nu_{Aj} \frac{\xi_j}{C_{A0}}$$

• YIELD
$$\phi_{PA} = \frac{n_P - n_{P0}}{n_{A0}} = \frac{C_P - C_{P0}}{C_{A0}} = \sum_j \nu_{Pj} \frac{\xi_j}{C_{A0}}$$

• SELECTIVITY
$$\psi_{PA} = \frac{n_P - n_{P0}}{n_{A0} - n_A} = \frac{C_P - C_{P0}}{C_{A0} - C_A} = \frac{- \sum_j \nu_{Pj} \xi_j}{\sum_j \nu_{Aj} \xi_j}$$

so it's right have
$$\boxed{\phi_{PA} = \psi_{PA} X_A}$$

We introduce also the differential selectivity
$$\sigma_{PA} = - \frac{r_P}{r_A}$$

The residence time is amount reaction time; for discontinuous reactors is REAL residence time, instead for continuous reactors is APPARENT ($\tau_0 = \frac{V}{q_0}$).

THERMODYNAMICS

In thermodynamic principles there are two variables: volume and pressure; with three main parameters which describe the systems (close or open): temperature, internal energy and entropy. In general it has
$$d(S^* + S_{ext}) > \delta Q \left(\frac{1}{T} - \frac{1}{T_{ext}} \right) > 0,$$

so the main law is
$$\boxed{dU^* = T dS^* - P dV^*}$$

In the same time there are energy variables:

$$dH^* = T dS^* + V^* dP$$
 enthalpy

$$dF^* = - S^* dT - P dV^*$$
 Helmholtz free energy

$$dG^* = - S^* dT + V^* dP$$
 Gibbs free energy

called THERMODYNAMIC POTENTIALS.

From the definition of these terms, they form two important relations:

Maxwell equations $\left(\frac{\partial T}{\partial V^*}\right)_S = -\left(\frac{\partial P}{\partial S^*}\right)_{V^*}$ or $\left(\frac{\partial S^*}{\partial P}\right)_T = -\left(\frac{\partial V^*}{\partial T}\right)_P$

Gilbs-Helmholtz equation $\left[\frac{\partial(G^*/T)}{\partial T}\right]_P = -S^*/T - G^*/T^2 = -\frac{H^*}{T^2}$

Therefore, it is possible to know

$$\begin{cases} dU^* = C_v^* dT + \left[T\left(\frac{\partial P}{\partial T}\right)_{V^*} - P\right] dV^* \\ dH^* = C_p^* dT + \left[V^* - T\left(\frac{\partial V^*}{\partial T}\right)_P\right] dP \end{cases}$$

depending only on T

where C_v^* and C_p^* are respectively the specific ~~heat~~ heat in constant volume and constant pressure.

Instead, for open systems, thermodynamic potentials depend on the variable number of moles n_i :

$$\begin{aligned} dU^* &= T ds^* - P dV^* + \sum_i \mu_i dn_i \\ dH^* &= T ds^* + V^* dP + \sum_i \mu_i dn_i \\ dF^* &= -S^* dT - P dV^* + \sum_i \mu_i dn_i \\ dG^* &= -S^* dT + V^* dP + \sum_i \mu_i dn_i \end{aligned}$$

when μ_i is chemical potential for each component

For hypothesis, at equilibrium, it has ~~the~~ $\sum_i \mu_i dn_i = 0$. It means that closed system with two phase α, β and component i present on both phases: $\mu_{i\alpha} = \mu_{i\beta}$.

$(\mu_{i\alpha} dn_{i\alpha} + \mu_{i\beta} dn_{i\beta} = 0$ and $dn_{i\alpha} + dn_{i\beta} = 0)$

Chemical potential ~~is~~ μ_i is defined ~~with~~ with $\mu_i = \mu_i^*(T, P) + RT \ln x_i$ called partial molar free energy, with μ_i^* molar free energy of pure component, defined as $\mu_i^*(T, P) = \mu_i^*(T, P_0) + \int_{P_0}^P V_i dP$. So the main equation is

$$\mu_i = \mu_i^*(T, P_0) + V_i (P - P_0) + RT \ln x_i \approx \mu_i^*(T, P_0) + RT \ln x_i$$

where x_i is the composition of gas i .

8

• PHASE RULE AND VARIANCE

A closed system with c components, f phases and r stoichiometrically independent reactions can be described by $c-1$ molar fractions per each phase, temperature and pressure. Therefore, $(c-1)f+2$ variables, and it has the following constraints: $(f-1)$ phase equilibrium equations per each component plus r reaction equilibrium equations, so $(f-1)c+r$ constraints.

It is defined Gibbs variance as $v_G = c - f - r + 2$.

Considering also extensive variables, we have $c \cdot f + 2 + r$ variables, and $cf + r$ constraints.

Therefore we define Duhem variance as $v_D = 2$.

• IDEAL SYSTEM: GAS PHASE

The equilibrium exists when $\sum_i \nu_i \mu_i = 0$ and, in gaseous phase,

$$\mu_i = \mu_i^\circ(T, P_0) + RT \ln\left(\frac{P}{P_0}\right) + RT \ln x_i = RT \ln P + RT \ln x_i + \mu_i^\circ(T)$$

therefore, $\sum_i \nu_i [\mu_i^\circ(T) + RT \ln P_i] = 0$ by Dalton law ($P_i = x_i P$)

We have ~~at constants~~ Gibbs energy as $\Delta G^\circ = \sum_i \nu_i \mu_i^\circ$ and all constants ~~are~~ described as:

equilibrium c. in terms of concentration $K_c(T) = \prod_i C_i^{\nu_i}$

equilibrium c. in terms of pressure $K_p = \prod_i P_i^{\nu_i} = \exp\left(-\frac{\Delta G^\circ}{RT}\right)$

equilibrium c. in terms of molar fraction $K_y = \prod_i x_i^{\nu_i}$

therefore $K_c = K_p \frac{1}{(RT)^{\nu}}$ and $K_y = K_p \frac{1}{P^{\nu}}$

→ dependence on temperature $\left(\frac{\partial \ln K_y}{\partial T}\right)_P = \frac{d \ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2}$

if $\Delta H^\circ > 0$, temperature and $K_p \uparrow$

if $\Delta H^\circ < 0$, temperature \uparrow and $K_p \downarrow$

→ dependence on pressure $\left(\frac{\partial \ln K_p}{\partial P}\right)_T = -\frac{\sum \nu_i}{P} = -\frac{\sum \nu_i V_i}{RT} = -\frac{\Delta V^\circ}{RT}$

if $\Delta M^\circ > 0$ ~~temperature and K_p~~ pressure \uparrow and $K_p \downarrow$

if $\Delta M^\circ < 0$ pressure and $K_p \uparrow$

• IDEAL SYSTEM: LIQUID PHASE

The equilibrium exists when $\sum_i \nu_i \mu_i = 0$ and, in liquid phase,

$$\mu_i = \mu_i^\#(T, P_0) + V_i(P - P_0) + RT \ln x_i \approx \mu_i^\#(T, P_0) + RT \ln x_i$$

therefore, $\sum_i \nu_i [\mu_i^\#(T) + RT \ln x_i] = 0$

We have Gibbs energy as $\Delta G^\# = \sum_i \nu_i \mu_i^\#$ and ~~the~~ equilibrium constant in terms of concentration is described as:

$$K_c(T) = \prod_i C_i^{\nu_i} = K_x C^\nu$$

→ dependence on temperature $\frac{d \ln K_x}{dT} = \frac{\Delta H^\#}{RT^2}$

if $\Delta H^\# > 0$ temperature and $K_x \uparrow$

if $\Delta H^\# < 0$ temperature \uparrow and $K_x \downarrow$

• REAL SYSTEMS

To real assessments there are two coefficients for describing of component ratios: for gas phase there is fugacity coefficient to correct partial pressure, for liquid phase there is activity coefficient to correct molar fraction.

→ To calculate the stoichiometry of reaction evolution, we follow some steps: given the operating conditions (T, P) and feed composition ~~the~~

+ calculation of the equilibrium constants at the given temperature;

+ calculation of the degrees of advancement at equilibrium at the given temperature, pressure and reactor feed composition;

+ calculation of the final compositions and yields.

⑧ With a non-stoichiometric approach, it is always right
Gibbs energy minimization $G^* = \sum_i \mu_i n_i$ ~~to~~ find
the equilibrium composition.

We have two constraints:

a.) mass conservation; the amount of each element must be the same in the input and output streams;

b.) non-negativity of the number of moles n_i .

~~type~~ For equilibrium model we have three inputs:

a.) input stream composition;

b.) temperature and pressure;

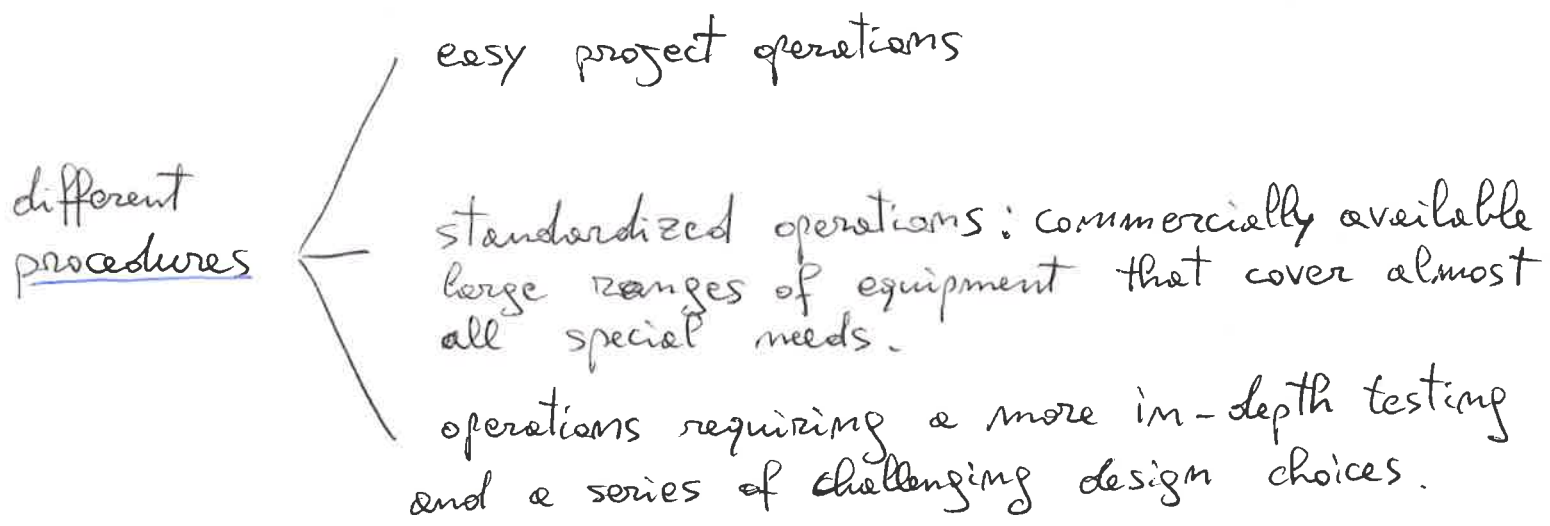
c.) output compounds.

But non reaction has to be considered.

PROCESS ANALYSIS AND DESIGN

The industrial process of development is regarding about many aspects of production and work:

- explorative research
- systematic laboratory research
- systematic research on a pilot scale
- optimal design of industrial equipment
- optimal construction of industrial equipment
- development of second-generation processes.



Every problem for development is based on some logic of optimization problems, such as the clear definition of the objectives and unambiguous quantification of them. Others crucial aspects are safety, quality of the work environment, social role of production, environmental protection and ecological balance.

By them, ~~they~~ there are more three problems:

- productivity, minimizing the size of the reactor
- selectivity, increasing the fraction of reactant converted into useful product.
- yield, maximizing the amount of product.

Reactors are classified ~~on~~ on the purpose of the reactor itself (laboratory, pilot or industrial), or also on the operating mode (batch, semi-continuous, continuous).

The discontinuous operating mode has some advantages that can be summarized as follows: easy of control, which is carried out by stopping the run at the desired time; great flexibility, each run can be performed according to production requirements; low installation cost.

The continuous operating mode is accomplished by means of open systems, generally at steady state, with continuous input of reactants and continuous discharge of the reaction products. The continuous operating mode allows for: lower operating costs, due to elimination of ~~the~~ the need for loading and unloading; the systematic adoption of automatic control; constancy over time of the reaction conditions and therefore uniformity of the product characteristics.

On semi-continuous operation mode, one or more reagents are loaded at the beginning, while others are made to flow continuously during operation.

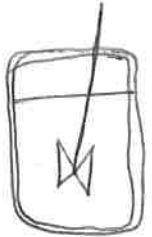
10 Reactors can be ~~be~~ classified ~~on~~ on number of involved phases

- homogeneous, in which the reagent phase ~~is~~ is unique, a liquid or gaseous mixture in which the kinetics ~~is~~ is not affected by mass and heat transport phenomena;
- heterogeneous, in which the phase are more than one, and the reaction involves the migration of chemical species ~~within~~ within the phases and between one phase and the other.

↳ Heterogeneous reactors could be classified on fluid-solid catalytic, ~~fluid-fluid~~ fluid-fluid, fluid-solid non-catalytic ~~reactors~~ or multi-phase reactors.

The most significant classification is based on the operating mode and the ways adopted to perform the reaction. We will discuss about DSTR, CSTR and PFR performances.

- DSTR, discontinuous stirred tank reactor, the measures are adopted to make the system as much uniform as possible. Little importance has the shape of reactor, while the main characteristics are "closed system" and "good stirring" of the reacting mass. The steps of reaction are considered instantaneous; all the chemical and physical-chemical variables are uniform over the whole volume of the reactor.



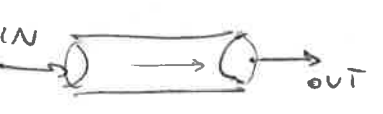
design equation: $t = \int_0^F \frac{P \cdot dF}{r(F)}$

- CSTR, continuous stirred tank reactor, it is designed for continuous operation and it can then run at steady state, in which the physical-chemical properties are also constant. It is fundamental the good agitation of the reacting mass by mechanical devices or due to the kinetic energy of the input streams.



The reacting fluid is assumed well mixed; to each variable a single instantaneous value is assigned, valid for all the points in the reactor, but possibly time-varying.

design equation $V = W \frac{F}{r}$

• PFR, plug flow reactor,

 the tubular reactors operate in a prevailing direction of flow, between input section and outlet section. In the reactor no device is used to promote mixing between successive transverse sections. ~~It~~ Assumed the uniformity in the cross section and the absence of axial diffusion phenomena.

design equation $dV = W \cdot \frac{dF}{r(F)}$

→ DYNAMIC ANALYSIS OF REAL ~~REACTORS~~ REACTORS

time parameters $\left\{ \begin{array}{l} \text{RESIDENCE TIME} - \text{interval of time between the input and the output (open system), as a rule in steady state} \\ \text{AGE} - \text{interval of time between the input and the present instant, with the fluid element still in the open system.} \end{array} \right.$

Therefore, the residence times ~~is~~ are the exit age.

• $F(t)$ integral distribution of residence time, represents the mass fraction of the outflow that has remained in the system for a time less than t ; it represents the probability that an element of the incoming fluid remains in the system for a time lower than t . $F(t)$ is dimensionless and satisfies the boundary conditions: $F(0) = 0$; $F(\infty) = 1$.

11. $f(t)$ differential distribution of residence time, is such that $f(t)dt$ represents the mass fraction of the outgoing flow that has remained in the system for a time between t and $t+dt$. It has the dimensions of the inverse of a time and from the definition follows that $f(t)dt = F(t+dt) - F(t)$

$$F(t) = \frac{dF}{dt} \quad F(t) = \int_0^t f(t) dt \quad \int_0^{\infty} f(t) dt = 1$$

$I(t)$ age distribution, is such $I(t)dt$ represents the mass fraction of the fluid system that has already spent in the system a time between t and $t+dt$. It has the dimensions of the inverse of a time and is similar to $f(t)$, but with one important difference: $f(t)$ summarizes a statistical survey made on the fluid exiting from the system, while $I(t)$ refers to the fluid in the system. $I(t)$ is related to the previous functions: if in the interval $0-dt$, Wdt is the mass entered into the system, at time $t-t+dt$ the fraction $1-F(t)$ still remains in the system. $(1-F)Wdt$ is mass with age between t and $t+dt$.

$$I(t) = \left(\frac{W}{m}\right) [1 - F(t)] \quad \int_0^{\infty} I(t) dt = 1$$

→ in IDEAL REACTORS ($t_m = \text{mean residence time}$)

DSTR: a single value of age at each instant and a single residence time. The functions $f(t)$ and $I(t)$ are Dirac functions and F is a step function

$$f(t) = \delta(t - t_m), \quad I(t) = \delta(t), \quad F(t) = \begin{cases} 0, & t < t_m \\ 1, & t > t_m \end{cases}$$

CSTR: differential distribution of residence times and ages coincide. They have the form of decreasing exponential. $F(t)$ is the complement to 1 of a decreasing exponential.

$$f(t) = I(t) = \left(\frac{1}{t_m}\right) \exp\left(-\frac{t}{t_m}\right), \quad F(t) = 1 - \exp\left(-\frac{t}{t_m}\right)$$

A cascade of n CSTR, each with mean residence time $t_{ms} = t_{mc}/n$ presents a $f(t)$, the more narrow the higher n

$$f(t) = \left(\frac{n}{t_{mc}}\right) \left(\frac{nt}{t_{mc}}\right)^{n-1} \left[\frac{1}{(n-1)!}\right] \exp\left(-\frac{nt}{t_{mc}}\right)$$

$f(t)$ tends to a Dirac function as n increases: for this aspect, the behavior of a cascade of many CSTR tends to coincide with the behavior of the ideal tubular reactor.

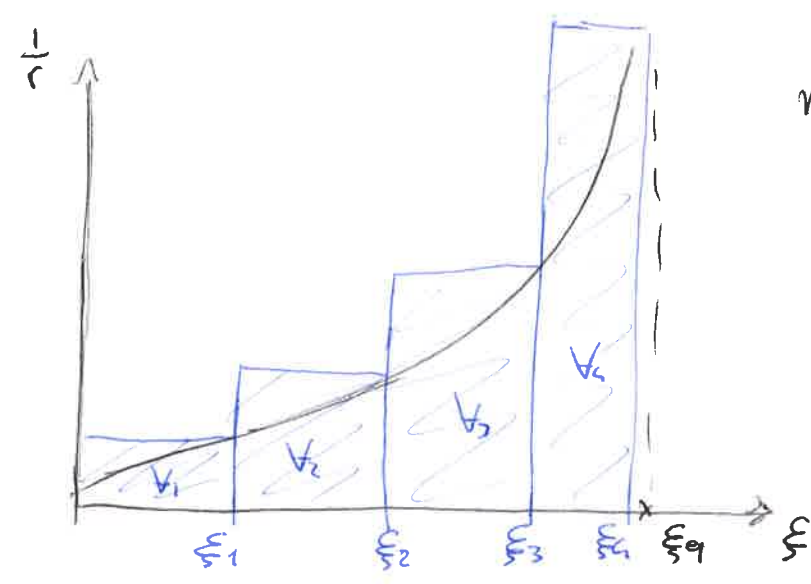
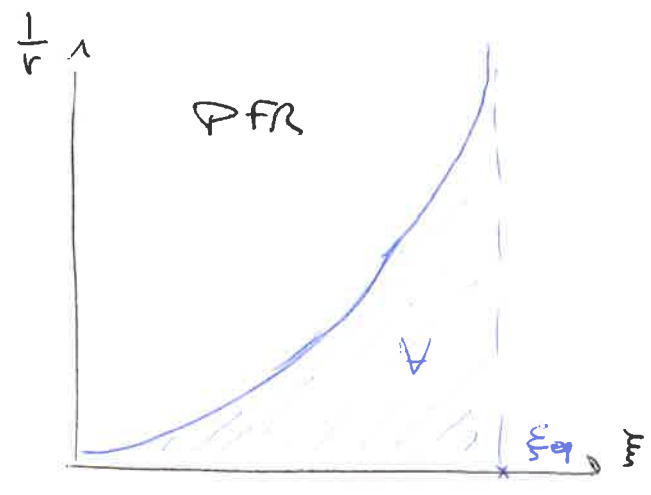
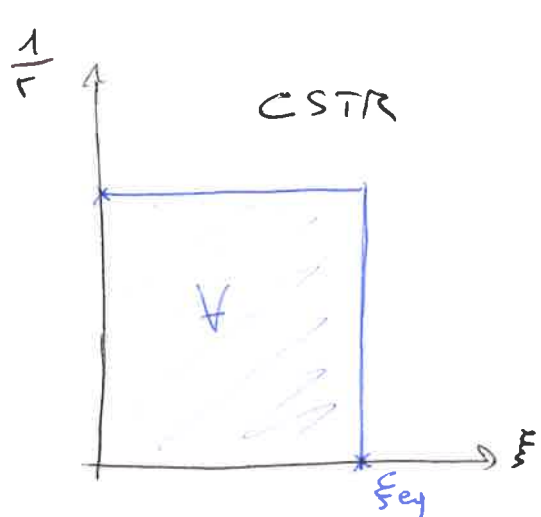
PFR: a single residence time: $f(t)$ is ~~the~~ a Dirac function and $F(t)$ is a step function.

$$f(t) = \delta(t - t_m) \quad F(t) = \begin{cases} 0, & t < t_m \\ 1, & t > t_m \end{cases}$$

All ages from zero (input) are equally frequent: $I(t)$ is a step function.

~~$$f(t) = \frac{1}{t_m} \delta(t - t_m)$$~~

$$I(t) = \begin{cases} 1/t_m, & t < t_m \\ 0, & t > t_m \end{cases}$$



(12)

COMBUSTION

Heat generation is from ligno-cellulosic biomass ~~with~~ through fireplaces, stoves, boiler. Power generation is from bio-oil, syngas, flue gas, biogas, ethanol, biodiesel through engines, turbines, fuel cells.

The main tools are steam turbines for solid biomass, which transform thermal energy in mechanical energy ~~and~~ to power; internal combustion engines for gaseous or liquid biofuels, which transform chemical energy in mechanical energy to power; fuel cells for biogas, syngas and ethanol, which transform directly chemical energy to power.

The ~~CHP~~ CHP is a generator of power and heat, (combined heat and power) in cogeneration.

The biomass inlet is selected by availability and price, physic-chemical characteristics, specific factors. For instance, it could be used waste (MSW), pellets (wood), dry biomass. Main attentions about sustainability of the whole chain, from production to final use.

The size of the storage system is about density ($\approx 400 \text{ kg/m}^3$), LHV ($8 \div 16,5 \text{ MJ/kg}$), moisture content ($10 \div 50\%$), plant nominal power, time to be warranted by the stored feedstock.

The useful volume of the silo must contain sufficient fuel to operate for the period that elapses between a supply and the next, plus a precautionary stock of the order of 20%. This volume must be determined in function of the consumption during that period of time, calculated in terms of maximum heat load.

$$V_{\text{MIN}} = \frac{E N a}{LHV \rho}$$

$$\begin{cases} E = \text{GS/day} \\ N = \text{day} \\ a = 1,2 \\ LHV = \frac{\text{GS}}{\text{m}^3} \end{cases}$$

The start-up of the wood burner could be manual, power assisted or with pilot burner using liquid fuels, in function of keeping the embers on during stand-by.

chips
boilers

- small - manual loading on the silo.
- medium - pneumatic ~~fills~~ loading.
- big - silo often below roadway level, to facilitate the unloading operations.

To correct storage of wood it is important follow some rules:

- halve the roundwood from 10cm in diameter;
- stacking wood logs in a ventilated place, possibly sunny, sheltered from the rain;
- stacking wood in logs, leaving sufficient gaps, so that the air circulation can eliminate the moisture produced;
- under the woodpile there must be an empty space, so that the moist air can flow;
- not deposit the freshly cut wood in storehouse, as air and sun are necessary for the drying;
- also the user of the heating system fueled by wood pellets must comply ~~at~~ with these directions, avoiding that wood would be stored in wet places.

Different kinds of ~~wood~~ heat generator are:

- open or closed fireplaces, are characterized by low thermal inertia and low efficiency and need for installation in areas with high air exchange;
- wood or pellet burning stoves, are characterized by high thermal inertia, given by the high mass of the stove, which then allows for easier placement and better heating;

13) wood, pellet or wood chips boilers, real heat generators, always warming the environment through a system of distribution of the heat generated.

A storage system consists of a water tank thermally isolated, directly connected to the boiler flow. It allows the boiler to operate smoothly, avoiding interruptions due to insufficient energy demand of the heating system. The uninterrupted operation reduces the smoke emissions and fouling of the fireplace, protects the boiler from the formation of condensed water and increases the overall performance of the system.

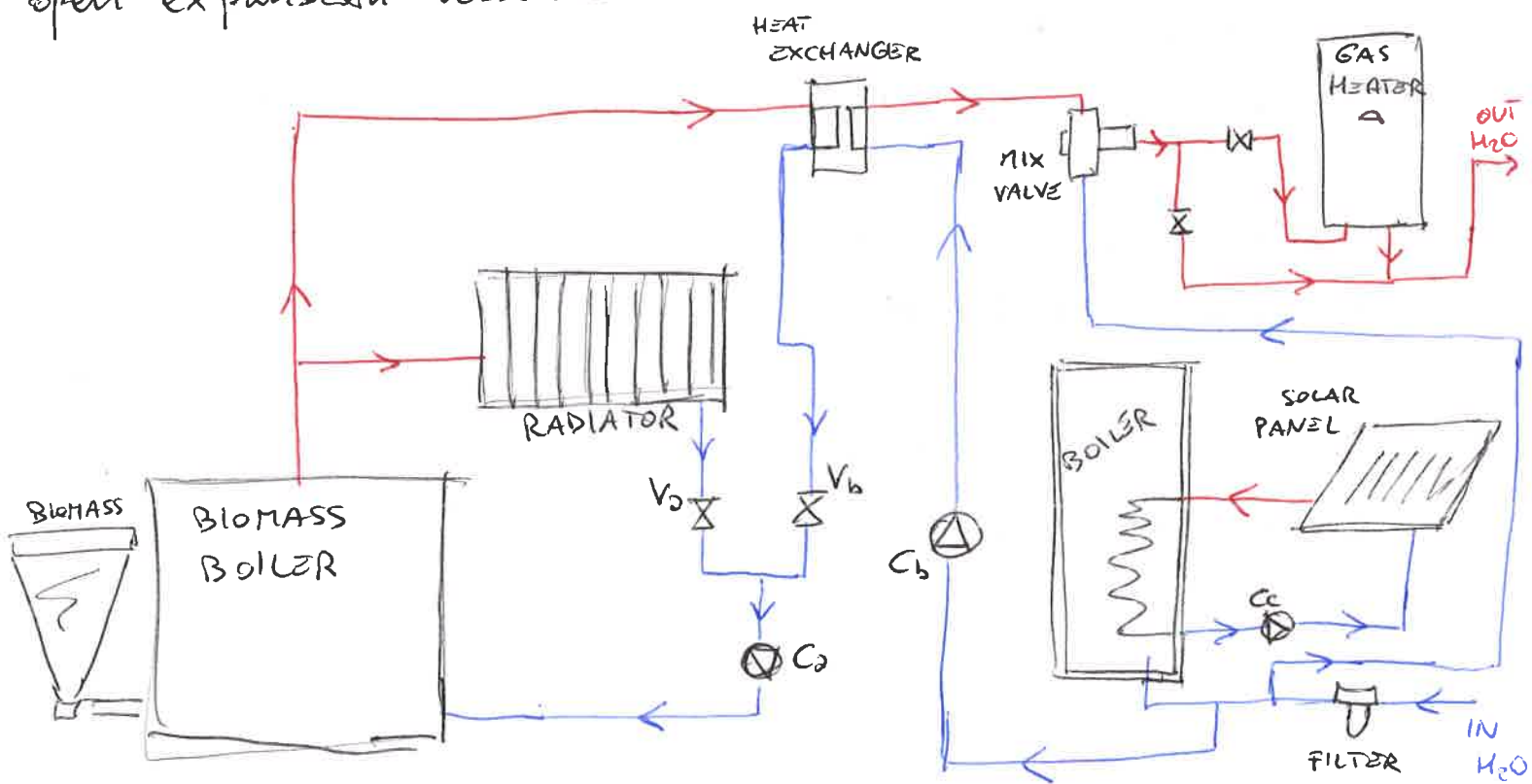
Some possible critical situations could be power outage and failure of the circulation pump of the boiler. In these cases the Block of the Circulation of the Water in the boiler occurs, and the water can reach boiling point, producing steam and abruptly increasing the pressure in the system. Therefore a heat discharge system is ~~used~~ utilized. It allows to prevent the water in the boiler to exceed a safety temperature. It is mainly used in systems with manual loading of the ~~solid~~ solid fuel, where it is not possible to stop instantaneously the combustion by deactivating the burner. With temperatures over the calibration values, this device discharges outside the hot water allowing ~~the~~ for the entrance of new cold water into the system. It returns to the close position when the water temperature returns to be acceptable.

If temperature of the water back to the boiler is too low, it may form corrosive condensate, with risk of boiler damage. So there anti-condensation devices are used.

HEAT GENERATION

A plant scheme for heat generation is composed by several kinds of elements with safety and reaction goals, such as thermometers, pressure indicators, valves, expansion vessel, circulating pump; ~~and~~ with separate loops with heat exchanger: one pump on the delivery to the space heating system, one pump on the delivery to the furnace. Three-way valves for mixing streams and adjusting delivery temperature.

Each part of scheme has a specific function, so there heat storage vessel is for better performances of the boiler, the heat exchanger separates water loops, domestic hot water is the heat exchanger almost mandatory, and the different loops ~~provide~~ provide an easier location of the open expansion vessels.



14) Therefore, the expansion vessel is one ~~of~~ for each water loop. Open expansion vessel of the water loop of the furnace. In addition, it will be necessary to insert safety valve, heat discharge valve and sensors, by law UNI 10412.

To design volume of heat storage it is used three methods:

- $V = 10 \times$ volume of combustion chamber
- $V = 60 \times$ nominal power of boiler [kW]
- $V = 15 \cdot t \cdot P \left(\frac{P_{min} - 0.3 \cdot P_{mc}}{P_{min}} \right)$ [EN 303-05]
with average power required (P_{mc}) and minimum boiler power (P_{min}).

On the primary loop, circulating pump always ON when the burner is ON, it is controlled ~~by~~ through variation of the fuel to the burner. The primary loop with open expansion vessel is connected with the upper part of the safety valve of the burner. Also there is a pipe for loading the expansion vessel with fresh cold water.

Chips burner is the feeding system which has to prevent the possible flame ~~back~~ back from the burner to the storage vessel. Often two screw conveyors at different level (one at the storage, one at the burner) with an intermediate hopper with a gate valve or a rotary valve. The flame ~~back~~ back is favored if the burner is in pressure, this is the system for controlling the pressure in the burner. Probes, safety, protection and control devices directly connected to the burner or in the delivery pipe.

Some control and protection systems are temperature manual reset or regulator, shut off valve, burner thermometer, delivery water thermometer, manometer, high pressure switch, vent,

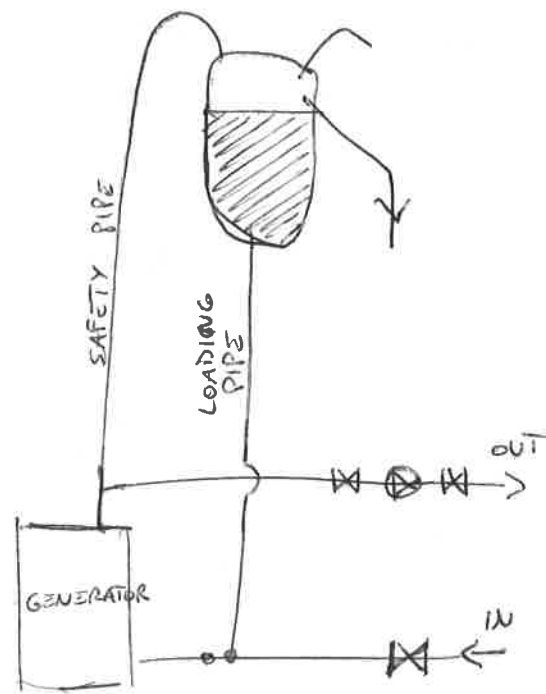
safety valve and expansion vessel. Instead, safety systems are automatic devices to prevent preset limit values of pressure and temperature are exceeded. For instance, safety pipeline connects the upper part of the heat generator with the atmosphere; safety valves automatically discharge a quantity of fluid such as to prevent that the predetermined safety pressure is exceeded; temperature relief valves automatically discharge a quantity of fluid such as to prevent that the predetermined safety temperature is exceeded; fuel shut-off valve automatically shuts off the flow of fuel in case of raising of the temperature of the water in order to prevent that the predetermined safety temperature is exceeded; self-activated shut-off valve of the primary fluid automatically intercepts the primary fluid in the heat exchangers in the case of the raise of the temperature of the secondary fluid so as to prevent that the predetermined safety temperature is exceeded.

Protection systems protect the burner before the safety devices go into operation. For instance, thermostat for regulation automatically ~~stopping~~ stops the fuel to the burner to the attainment of a predetermined limit temperature of the water and to restore it only after the lowering of the temperature below the above limit; high pressure switch automatically stops the fuel input to the burner to the attainment of a predetermined pressure limit of the water; low pressure switch automatically ~~stops~~ ensures that the pressure in the burner never falls below a certain value in order to prevent the vaporization of water.

Open expansion vessel consists of a container having a parallelepiped or cylindrical shape and equipped with a cover to prevent foreign bodies to get in, and a level sensor. Below the medium level an automatic system allows

15) water entering the vessel, while above the maximum level the water is discharged through an overflow. The heat generator must be connected to a safety pipe and to a loading pipe. There may be a connection between the safety pipe and tube loading, to ensure the circulation by gravity. The loading pipe connects the bottom of the generator with the bottom of the expansion vessel in order to allow the

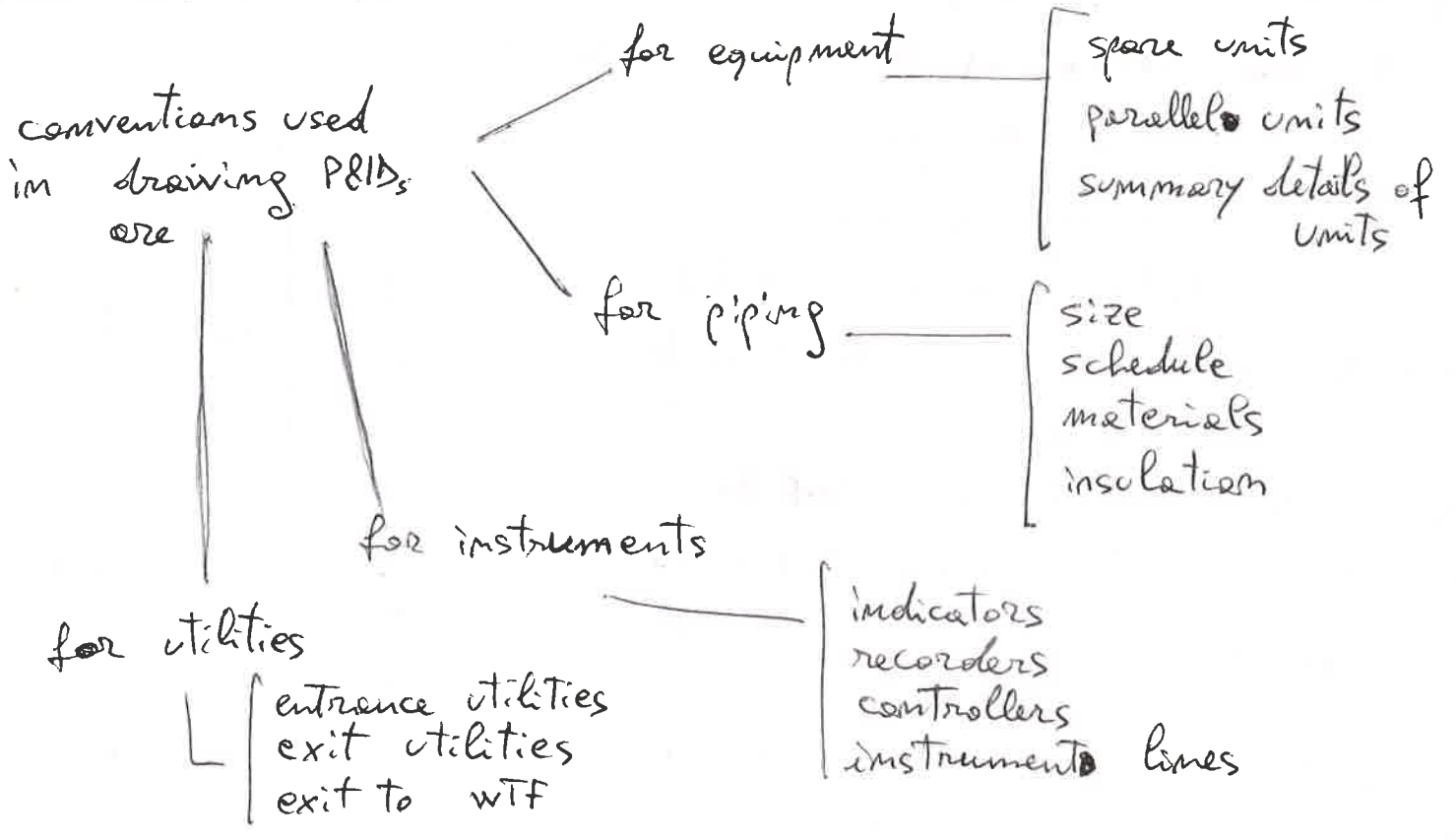
rapid filling of the generator with the water coming from the vessel. A filling pipe is connected directly to the expansion vessel or to the lower part of the loading part. The safety pipe must be connected to the highest part of the generator with the atmosphere and should not present counter-slopes, except in its upper part where it reaches the expansion vessel.



Closed expansion vessel is a small container divided in two by a rubber diaphragm. One side is connected to the pipe work of the heating system and therefore contains water. The other dry side contains air under pressure, and normally a valve system for checking pressure and adding air. When the heating system is empty or at the low end of the normal range of working pressure, the diaphragm is pushed against the water inlet; as the water pressure increases, the diaphragm moves, compressing the air on its other side.

PIPING AND INSTRUMENTATION DIAGRAM

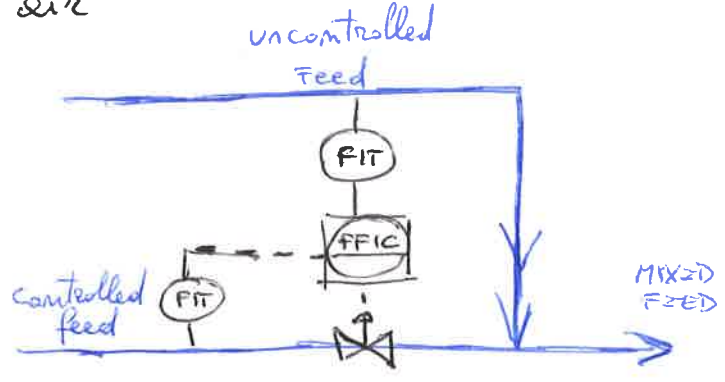
P&ID provides information needed by engineers to begin planning for the construction of the plant. It includes every mechanical aspect of the plant ~~except~~ except the information of operating conditions, stream flows, equipment locations, pipe ~~rough~~ routing, supports, structures, and foundations.



All processes information that can be measured on the plant is shown on the P&ID by circular flags. This includes the information to be recorded and used in process ~~loop~~ control loops. The circular flags on the diagram indicate where the information is obtained in the process and identify the measurements taken and how the information is dealt with.

In steam generator, control of the air and fuel mixture is crucial to maintaining a safe and efficient combustion in the boiler.

RATIO CONTROL:



16) BIOGAS

Biogas is combustible mixture of gases formed from the anaerobic bacterial decomposition of organic compounds, such as carbohydrates (cellulose, hemicellulose, starch), fats and proteins.

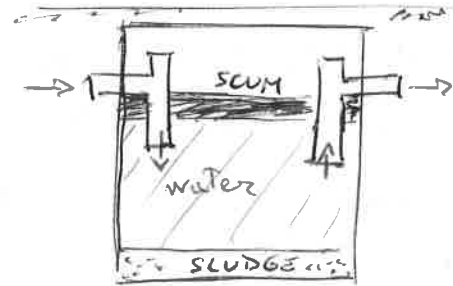
Biogas is produced naturally in swamps, rice paddies, and in sediments at the bottom of lakes and oceans. Methane (CH_4) is also created in the rumen of ruminant animals (cows, sheep...)

greenhouse effects



~~permafrost~~ permafrost thawing
 CH_4 release

First Biogas system had septic tank for waste water treatment, still used for isolated properties where there is no sewerage system. But the Biogas is not collected.



~~1850~~ In 1850 septic tank with gas collection, which used for street lighting. In ~~1850s~~ 1850s Biogas plants for waste water treatment produced gas to heat the plant's digester tank. WWTP intended for decomposing the organic matter in the wastewater and thus reduce and stabilize the sludge, not for energy recovery.

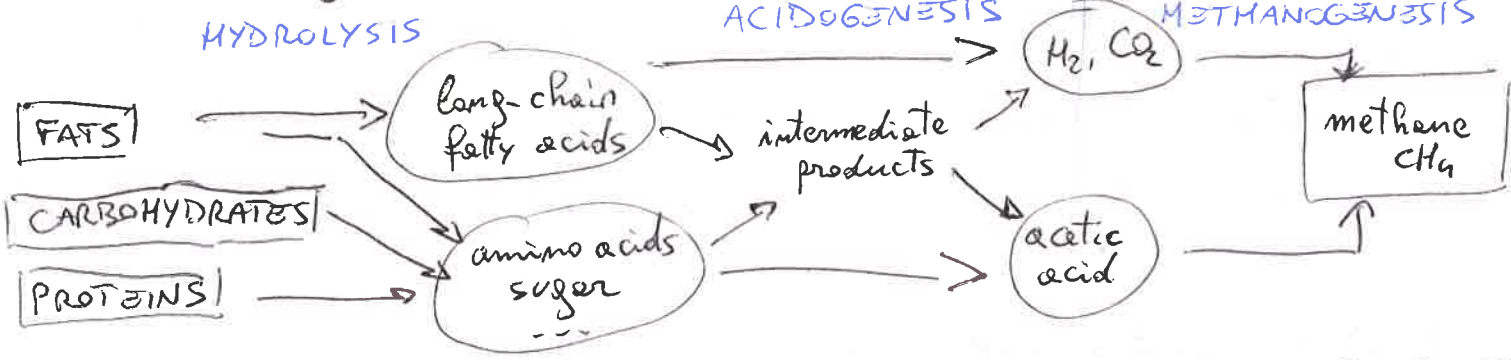
Biogas industry started to develop in Germany, Britain and France, addressing agriculture and energy recovery till the end of 1850s. The development stopped and started again after 1873 with animal manure as the main feedstock. Today Biogas plants are intended for ENERGY RECOVERY and NUTRIENTS RECYCLING to the agricultural sector.

ANAEROBIC DIGESTION

Anaerobic digestion is the reaction of organic matter without oxygen, through bacteria:



It is composed by three phases: hydrolysis, acidogenesis (fermentation) and methanogenesis.



• HYDROLYSIS: is the process to transform long chain molecules to small molecules, such as Glucose, xylose, amino acids, long chain fatty acids (LCFA).

• ACIDOGENESIS: is the process to transform LCFA's to acids, such as acetic acid CH_3COOH (50%), CO_2 and H_2 (20%) and short chain volatile fatty acids VFAs (30%).

The relative VFA can increase, if it accumulates the process can be inhibited, in fact it is a limiting factor for the biomass process.

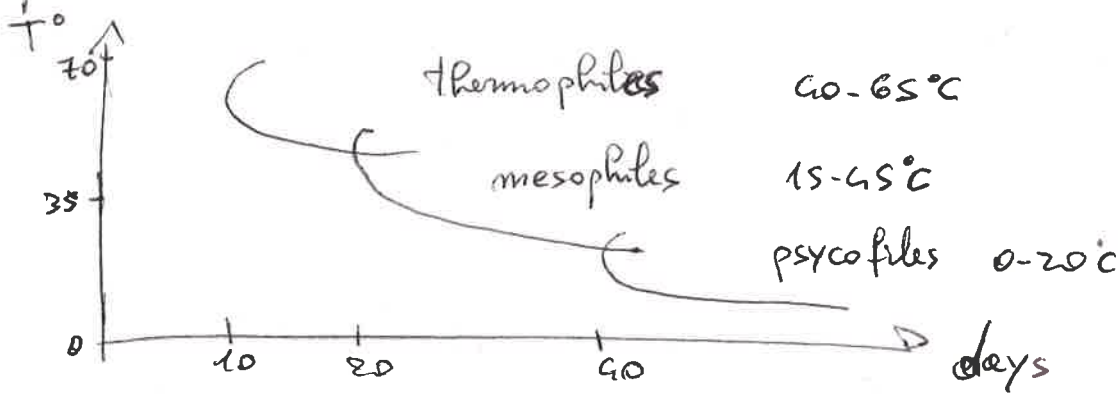
• METHANOGENESIS: is the process to transform acids to methane CH_4 . It could be named Met.1 if acetic acid makes CH_4 , and Met.2 if gases CO_2 and H_2 makes CH_4 . These processes are balanced (70% and 30% respectively) for avoid inhibition.

The inhibition of methanogenesis could be due to large amount of fats in the feedstock (so LCFA's) or large amount of proteins (so ammonium or ammonia).

The limiting factor is the growth of bacteria ratio which involves in the process.

(17) Because an anaerobic biogas plant is well done, ~~it needs~~ ~~it needs~~ about some parameters!

- ANAEROBIC ENVIRONMENTS, therefore, the methanogenesis needs an oxygen-free environment; the bioreactor should be airtight.
- TEMPERATURE, which increases with the rate of biochemical processes. This applies to the biogas process where, actually, several types of or strains of bacteria can be involved and adapted to the different temperature.



- ACIDITY, around $6.5 \leq \text{pH} \leq 8$ for balanced production of acids (acidogenesis). The buffer capacity in the biogas reactor is very large, and it takes a lot to alter it: the system is very robust and stable. Slurry based plants often have a somewhat higher pH due to a higher ammonium content.
- SUBSTRATE, ~~it~~ is composed by organic matter, but lignin is indigestible.
- COMMINATION, the material has the maximum of relative surface, because it is easier to be attacked by bacteria.
- DRY MATTER CONTENT, best conditions are $\text{dm} \leq 50\%$ and usually, in a biogas plant, $\text{dm} \leq 10\%$.
- C/N RATIO, it is represented by micro/macro nutrients to proteins production. Often it is $\text{CN} < 30$, if N is lower ~~it~~ it became the limiting factor, but if N ~~is~~ is too high, the process is inhibited.

- STIRRING, it means the method of reactor to mix the biogas and ~~the~~ favouring the methanogenesis.
- ORGANIC LOAD, because it is the most important factor of process. The rate ~~of the~~ at which biomass is added to the reactor has to be adjusted to the growth rate of the methanogenesis and organic acids have to be removed at the rate at which they are produced. COD represent the amount of oxygen needed to degrade organic matter in water to CO_2 and H_2O . It is commonly expressed in mass of oxygen consumed over volume of solution $\left[\frac{\text{mg O}_2}{\text{L}}\right]$.

When a substance has a negative effect on bacteria without directly killing them, we have an inhibition, it could be endogenous (due to material) or exogenous (due to external conditions).

If the organic acids formed during the process are not removed as soon as they are formed, it has an acidification, so endogenous inhibition.

In the same time, antibiotic and disinfection agents are exogenous inhibitions. They are used in livestock production and ~~thus~~ thus can be found in the slurry, but usually at concentrations so low that they do not have a negative impact on the biogas plant. A slow adaptation to these substances can also take place if the supply is fed continuously. Heavy metals, salts and micronutrients can also inhibit the process at high concentrations.

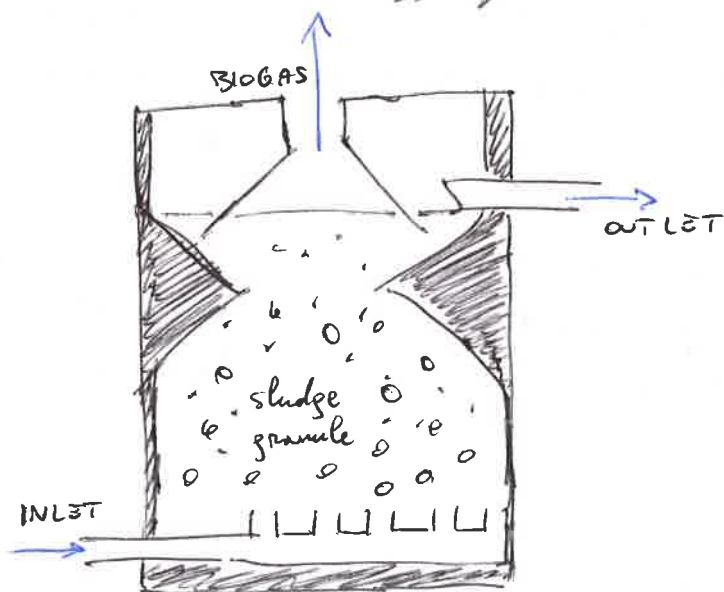
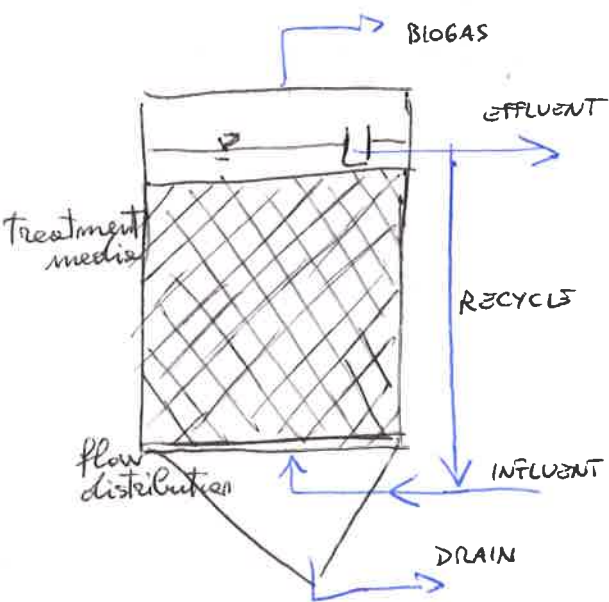
18) Some kinds of anaerobic digester ~~and~~ could be:

- ANAEROBIC FILTER

Mostly used in sewage treatment systems. An anaerobic filter is a fixed-bed biological reactor with one or more filtration chambers in series. As wastewater flows through the filter, particles are trapped and organic matter is degraded by the active biomass that is attached to the surface of the filter material.

- Upflow Anaerobic Sludge Blanket reactor

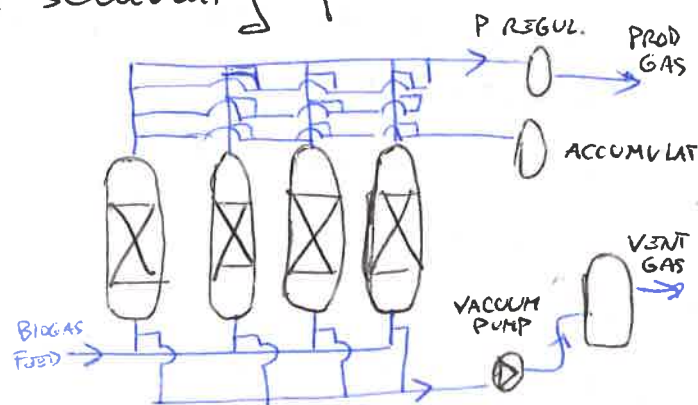
It uses an anaerobic process whilst forming a blanket of granular sludge which suspends in the tank. Wastewater flows upwards through the blanket and is degraded by the anaerobic microorganisms. The upward flow combined with the settling action of gravity suspends the blanket with the aid of flocculents. The blanket begins to reach maturity at around three months. Small sludge granules begin ~~from~~ to form whose surface area is covered in aggregations of bacteria.



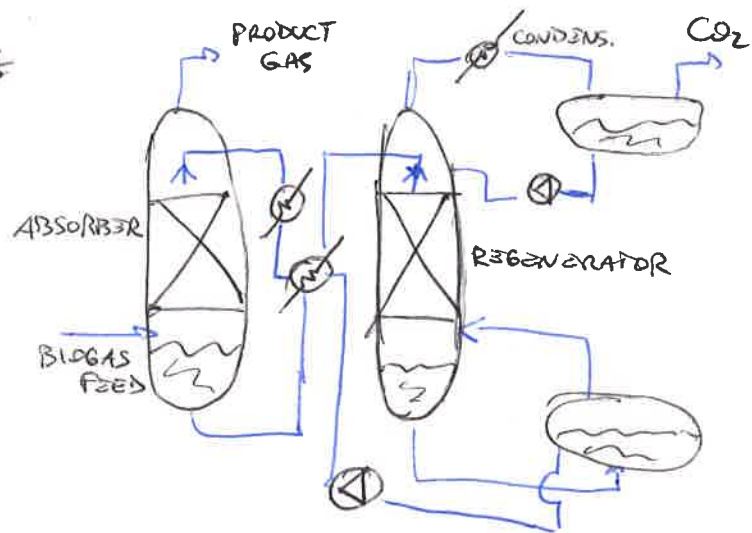
SYNTHETIC NATURAL GAS (SNG)

To produce C_{10} for use in an internal combustion engine and power generation, operators usually do not remove CO_2 from the biogas. However, for injection into the city gas network, the biogas needs to meet stringent specifications and CO_2 has to be removed. In the case where the gas will be liquefied, CO_2 has to be removed to ppm level. The most commonly used for biogas ~~app~~ applications are vacuum pressure swing adsorption (VPSA) or multistage membrane system. In case where ppm levels of CO_2 are required, amine scrubbing process is used.

- VPSA, biogas is passed through a bed made of specific adsorbent. CH_4 goes through the bed and all other impurities including CO_2 are ~~also~~ adsorbed by the bed media.



- AMINE SCRUBBING, refers to ~~biogas~~ processes that use aqueous solutions of various alkyl-amines to remove H_2S and CO_2 from gases. The resultant rich amine is then routed into the regenerator to produce regenerated or lean amine that is recycled for reuse in the absorber.



19 CASE STUDY

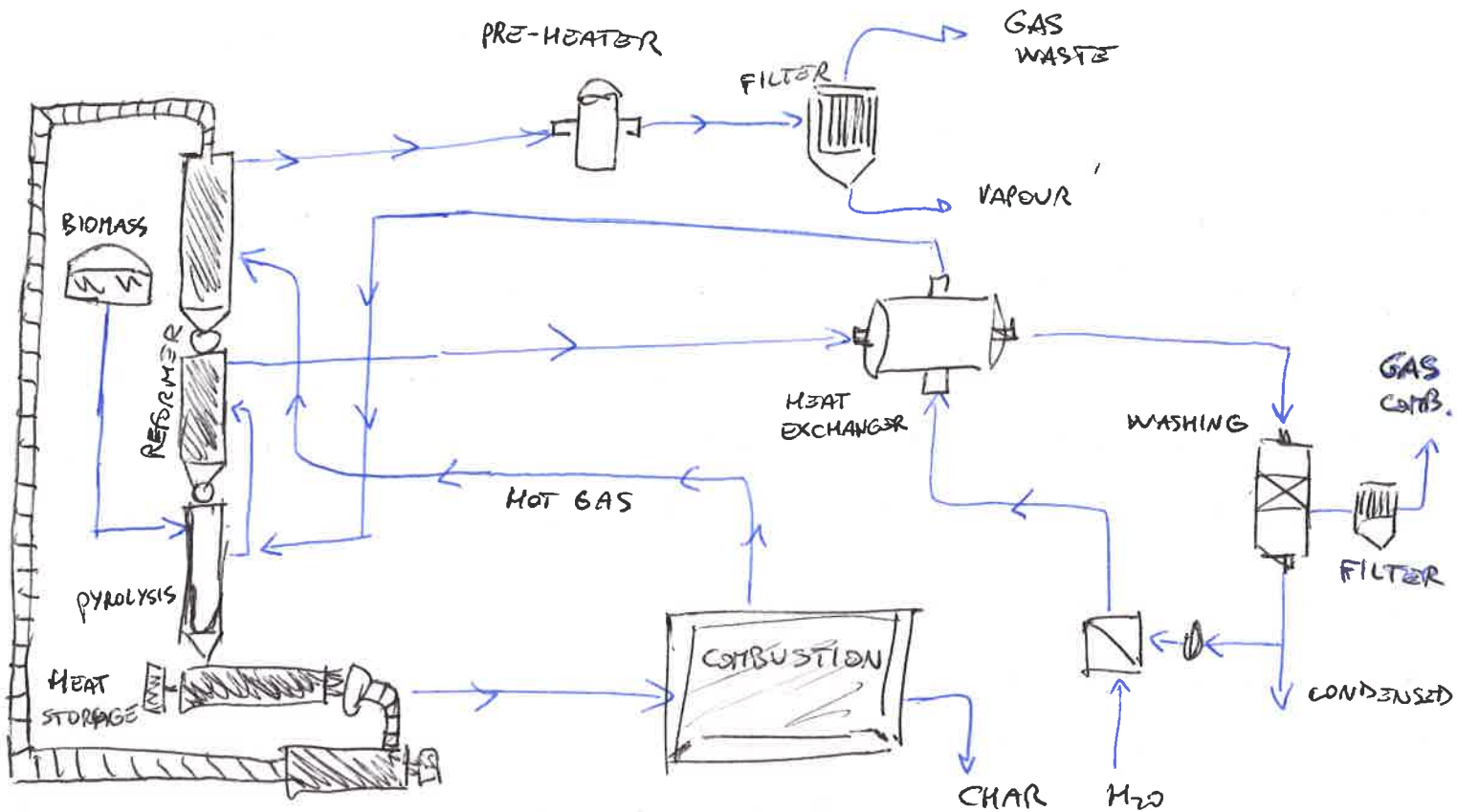
1. THE BLUE TOWER GASIFICATION PLANT (2008)

It is located in Germany (Herten), it costed 26M€ and ~~high~~ is high 42m. It uses 48000 $\frac{\text{ton}}{\text{year}}$ roadside greenery ~~input~~^{as} input material to generate ~~13~~ 13 MW and produce 150 $\frac{\text{m}^3}{\text{h}}$ H_2 , with approximately 37500 MWh/year of power. It reduces fossil fuel about 17.8 million m^3 of natural gas/year with an emission of 15.3 million tonnes of CO_2 /year avoided.

Green H_2 is produced by means of staged reformation in the Blue Tower. In detail, this means that at temperatures of around 600°C green cuttings are thermally decomposed and converted to a level of 80% into a gas. The remaining solids are transformed into coke, which can in turn be used to generate the required process heat. The resulting gas is refined with steam at approximately 850°C to form a very hydrogen-rich "Blue Gas". It is processed into pure H_2 or used in gas engines for the production of electricity. The heat required for the thermal decomposition and refinement of the gas is supplied via heated ceramic beads, which migrate through the process and give off their heat.

The above-mentioned coke is combusted to heat the beads. ~~With a thermal input of 13 MW the Blue Tower in Herten supplies 150 m^3 of H_2 an hour and~~

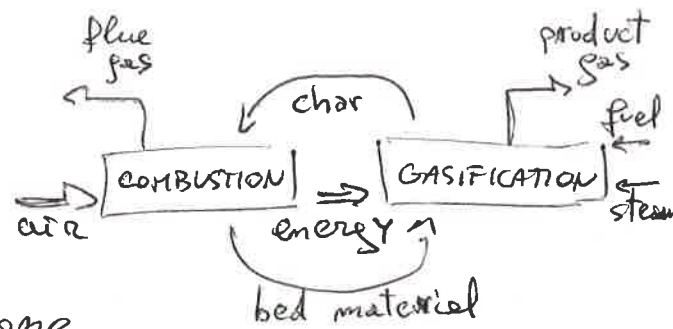
The principle of operation is based on PYROLYSER, which includes only biomass feeded through thermolysis (500°C) with 20% of char; an STEAM REFORMER, supplied by pyrolysis gas and steam. A syngas of H_2 is produced; an COMBUSTOR, supplied by char and air at high temperature; an PREHEATER, supplied by ceramic beads and flue gas; and a SYSTEM FOR LIFTING, -



The two-stage process is formed by pyrolysis and steam reforming: the syngas from the reformer present very low amount of high weight hydrocarbons. There is an indirect heating, due to the absence of N_2 in SNG.

2. THE FICFB TECHNOLOGY BY EDF IN GÜSSING

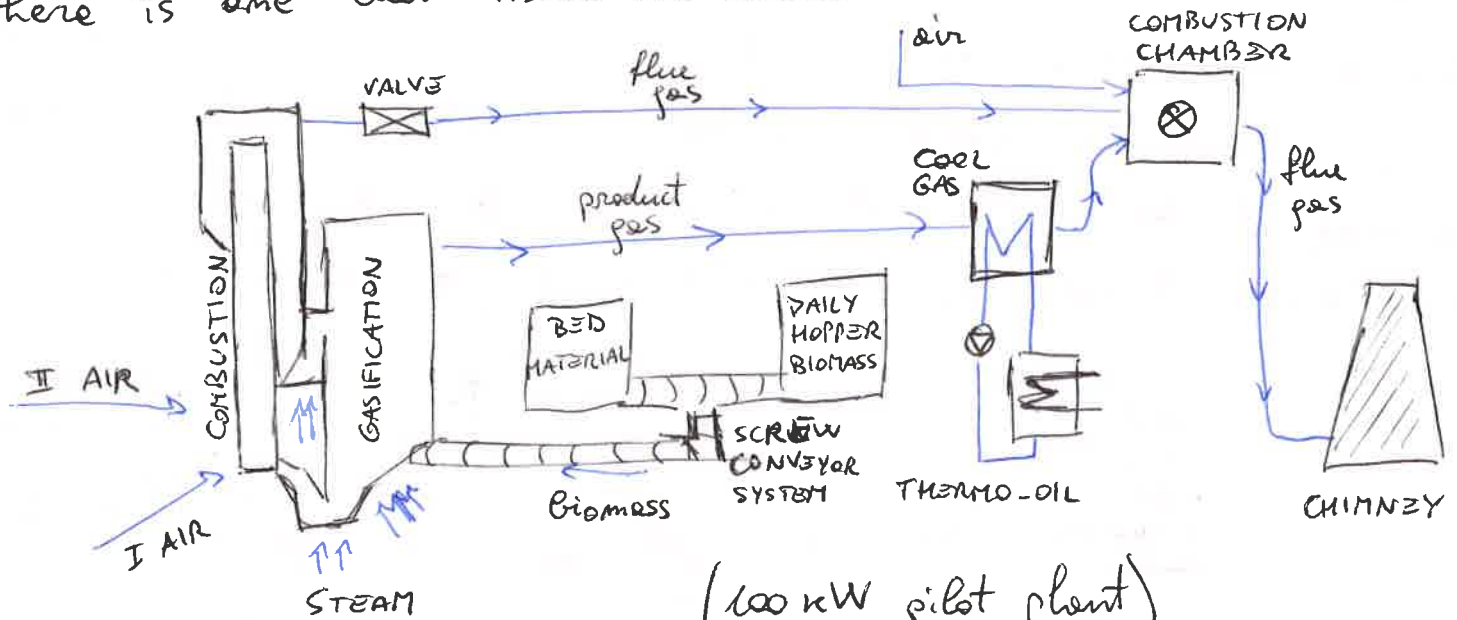
The basic idea of the gasification process is the fluidization of bed reactor with indirect heating.



The fuel is fed into the gasification zone and gasified with steam. The gas produced in this zone is therefore nearly free for N_2 . The bed material, together with some charcoal, circulates to the combustion zone. This zone is fluidized with air and the charcoal is partly burned. The exothermic reactions in the combustion zone provides the energy for the endothermic gasification with steam. Therefore the bed material at the exit of the combustion zone has a higher temperature than at the entrance.

② The flue gas will be removed without coming in contact with the product gas. With this concept it is possible to get a high-grade product gas without use of pure oxygen. This process can be realized with two fluidized beds connected with transport lines or with an internally circulating fluidized bed.

• FICFB: Fluidized bed + circulating fluidized bed, it means there is one bed inside the other.

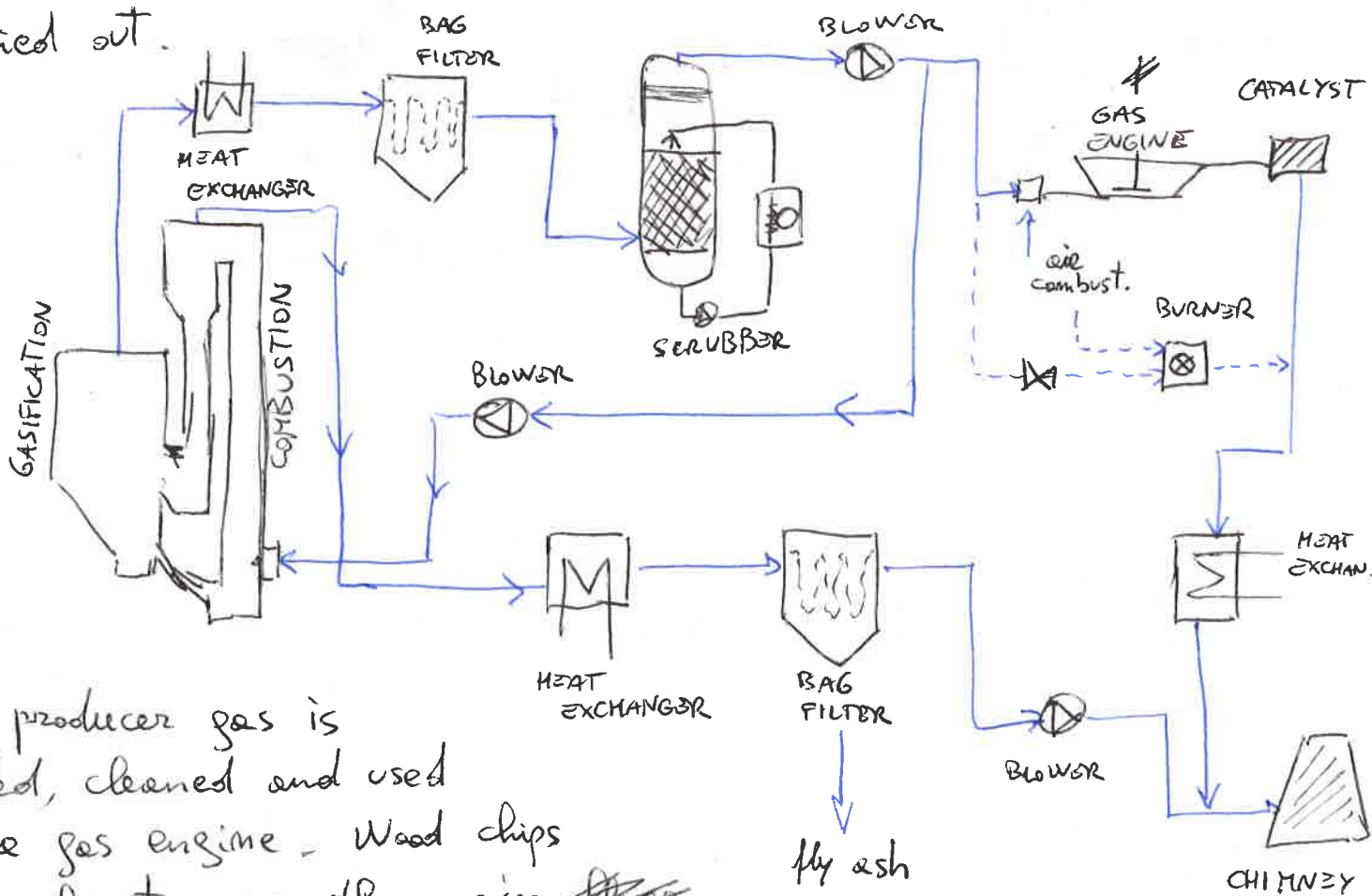


• TCFB: twin circulating fluidized bed, with transport lines.

The FICFB gasifier has the following main advantages compared with an air blow gasifier: product gas nearly free N_2 , calorific value higher than 13 MJ/Nm^3 , very low tar content due to steam gasification, gas quality is independent of water content in biomass feed, the apparatus is very compact, a wide range of feedstock can be gasified, possibility to use a catalyst as bed material to influence the gas composition and gasification kinetics in a more positive way. The main disadvantages are that there is erosion, due to the circulation of material, and there are two reactors.

3. 8 MW BIOMASS CHP IN GÜSSING

In the year 2002 a 8 MW CHP plant based on a circulating fluidized bed steam blown gasifier producing heat and power with a gas engine went into operation in Güssing (AUT). Due to the ~~excellent~~ excellent performance that was reached during the last year, several additional research project have been started in Güssing. The producer gas from the circulating allothermal fluidized bed gasifier is nearly ~~free~~ free of N_2 and has an high H_2 content. For this reason it is well suited for fuel cells as well as several synthesis products. Therefore, projects aiming at the development of processes for the production of synthetic natural gas and Fisher-Tropsch liquids are currently carried out.

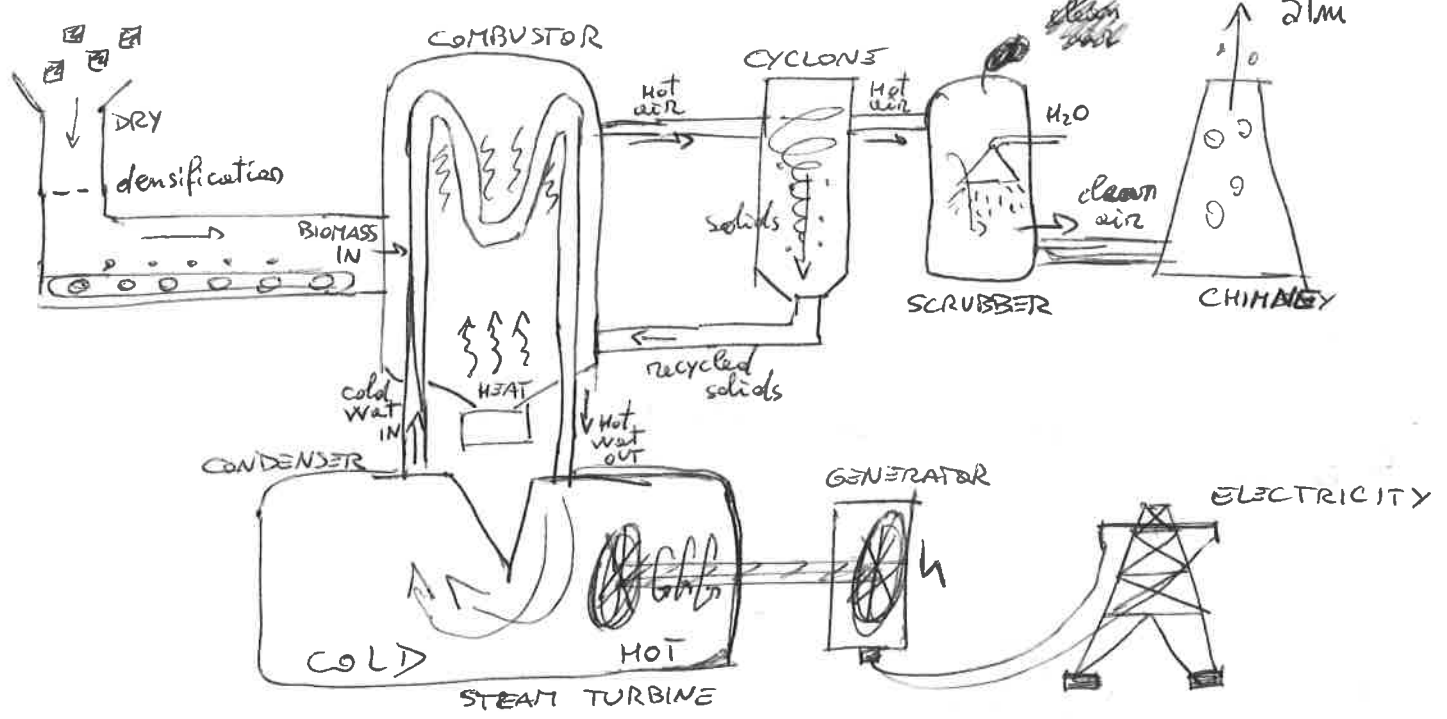


The producer gas is cooled, cleaned and used in a gas engine. Wood chips from forestry are the main ~~fuel~~ fuel for the demonstration plant. The wood trucks are dried naturally by storage of about 1-2 years in the forest. Then they are delivered to the CHP-plant and chipped there. When

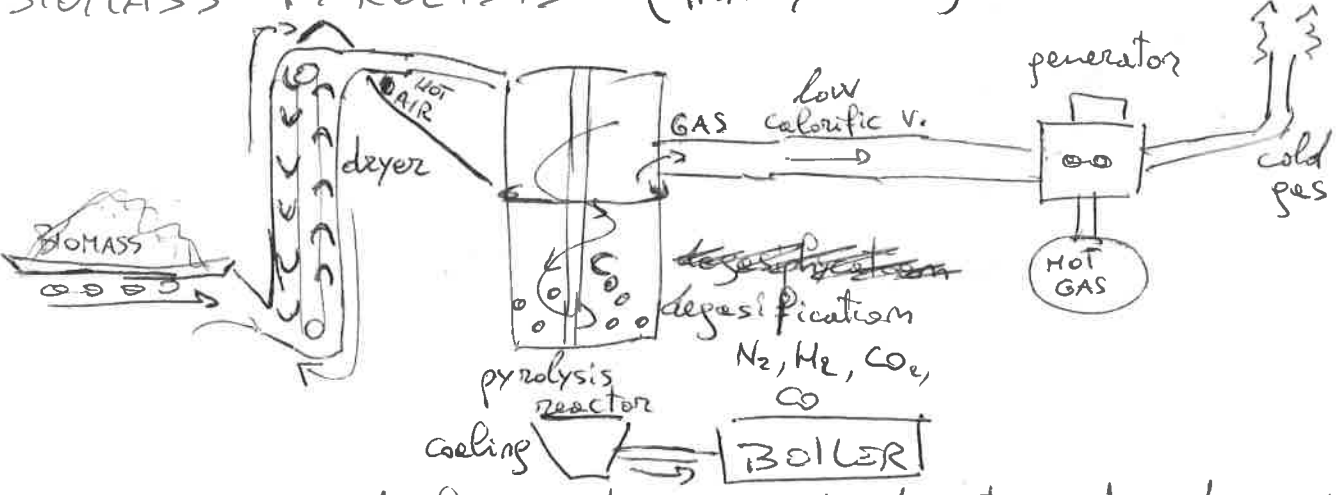
(21) The biomass is used, it has a water content of about 25-40%. The heat produced in the process is partly internally used, and the rest is delivered ~~to~~ to an existing district heating system. The net electricity produced is delivered to the electrical grid. Since the beginning of operation of the demonstration plant the improvement and optimisation of the operation performance was a permanent task. This optimisation work leads to a reduced amount of operation means and also a reduction of waste material which means ~~over the last years~~ fly ash from the flue gas line. ~~The following figure shows the development of the main operation means over the last years.~~

It is clear that the availability of any demonstration plant can not be as high as for a plant ~~which~~ which uses an already mature technology. For such an innovative technology as it is used in the case of the FICFB allothermal steam gasification plant and the gas cleaning system several years of operation experience are necessary to remove all the weak points within the plant.

COMBUSTION (from youtube)



BIOMASS PYROLYSIS (from youtube)

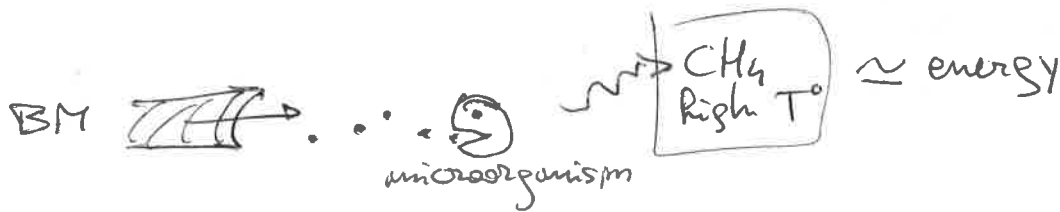
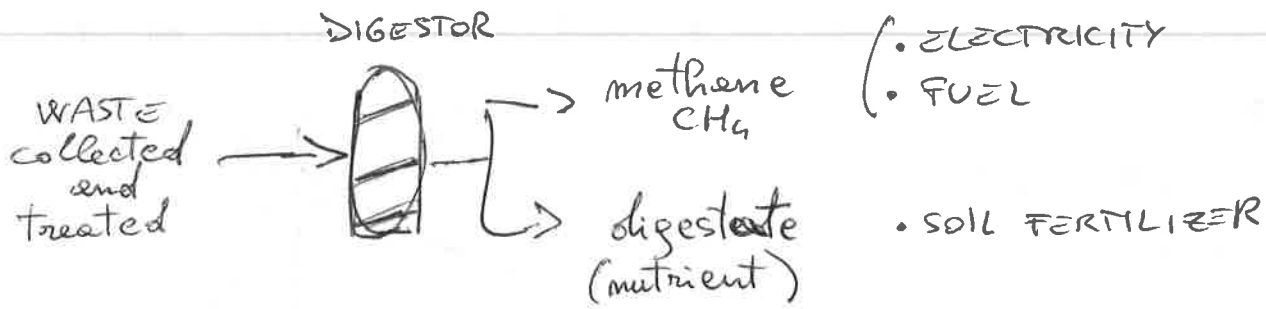


Biomass pre-dried has positive impact due to reduced moisture. The efficiency is maximized with hot air inlet to drier.

ANAEROBIC DIGESTION (from youtube)

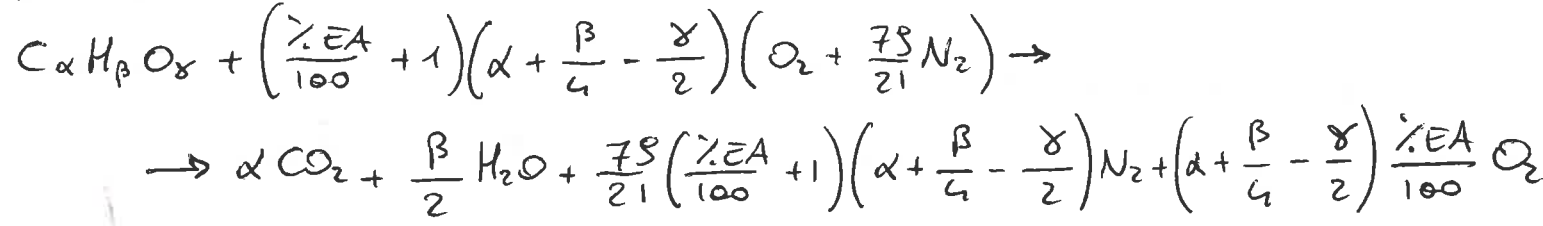
It is a series of biological processes in which microorganisms break down biodegradable material in the absence of O_2 .

Anaerobes ~~are~~ excess oxygen from sources other than the ~~surrounding~~ surrounding air. The oxygen source ~~the~~ for these microorganisms can be the organic material itself or alternatively may be supplied by inorganic oxides from within the input material.



COMBUSTION is a chemical reaction of a fuel and an oxidant agent. It is an exothermic process.

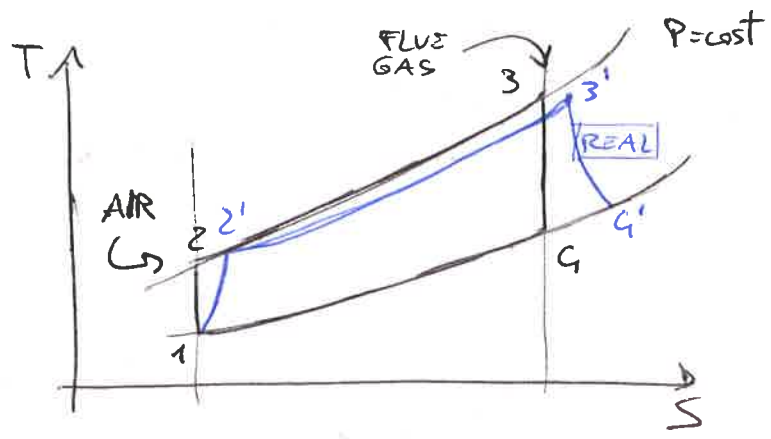
For a lean combustion:



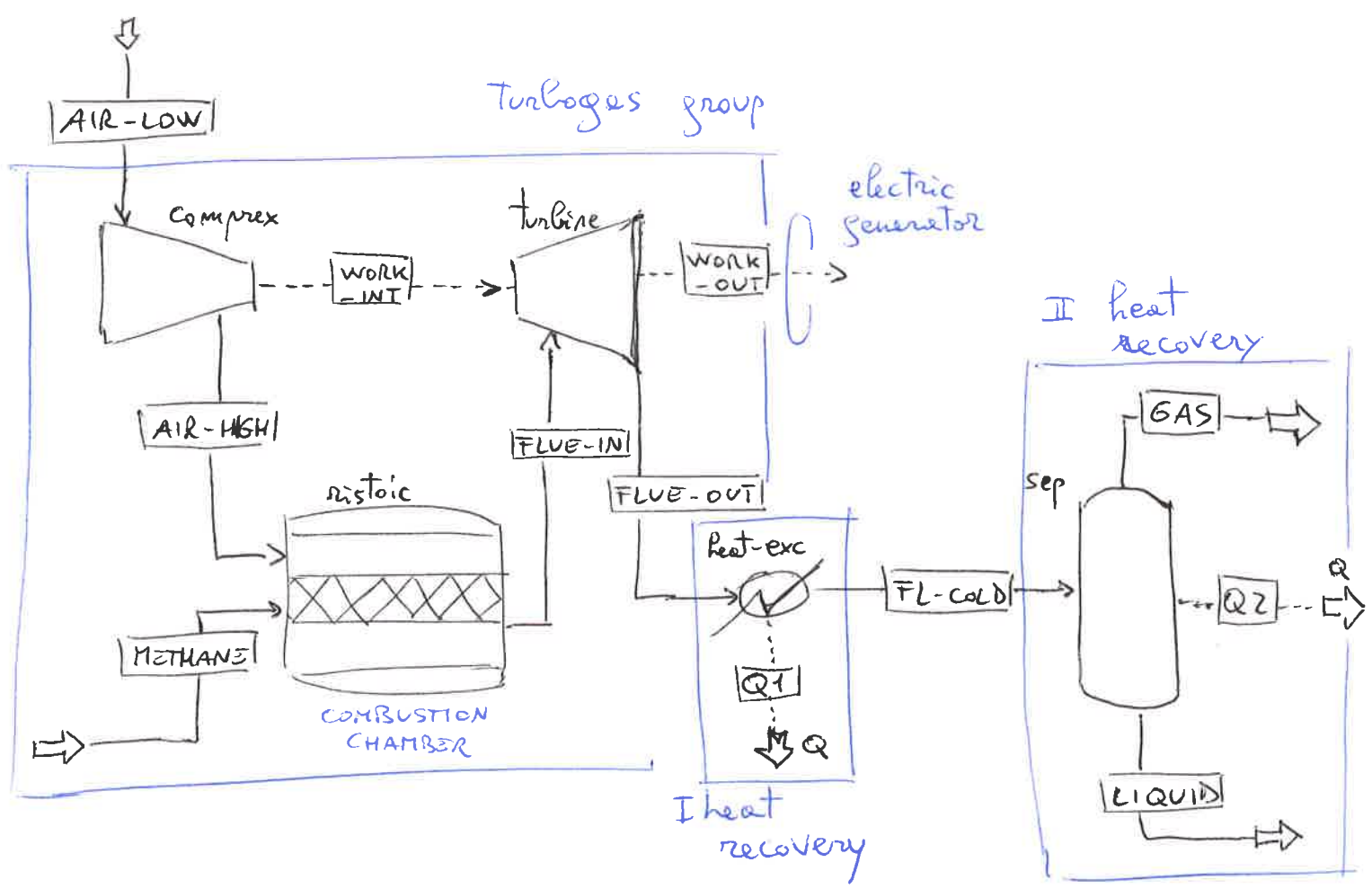
where $\%EA = \left(\frac{m_{air}}{m_{air,s}} - 1\right) 100$ excess of air

COGENERATION PLANT = combined heat and power CHP: electrical/mechanical energy and heat are produced at the same time.

TURBOGAS, with Joule-Brayton cycle



- 1-2': compression of air
- 2-3': heat from the combustion
- 3-4': expansion in turbine of flue gas



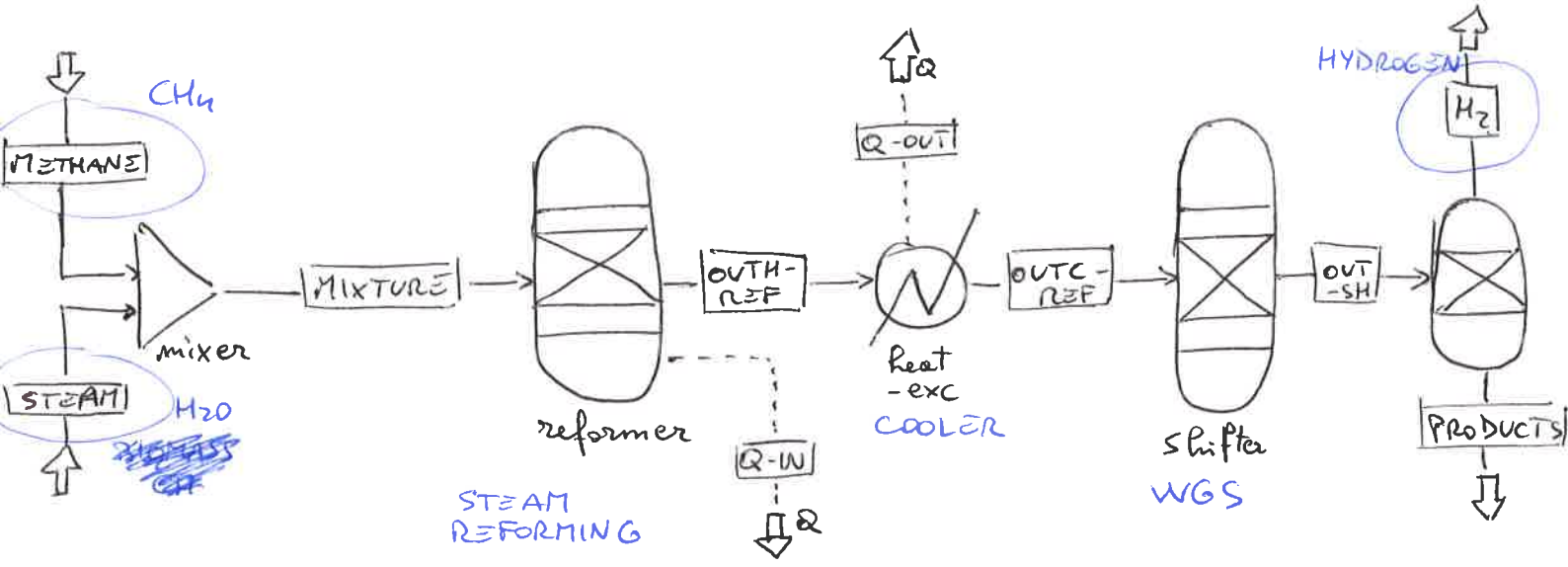
STEAM METHANE REFORMING is a method used industrially for the production of hydrogen either as a pure gas or as a reactant for the production of ammonia or methanol. The process involves the reforming of natural gas in a continuous catalytic process. The main reaction involves the formation of H_2 , CO and CO_2 from CH_4 and steam.

REACTIONS:

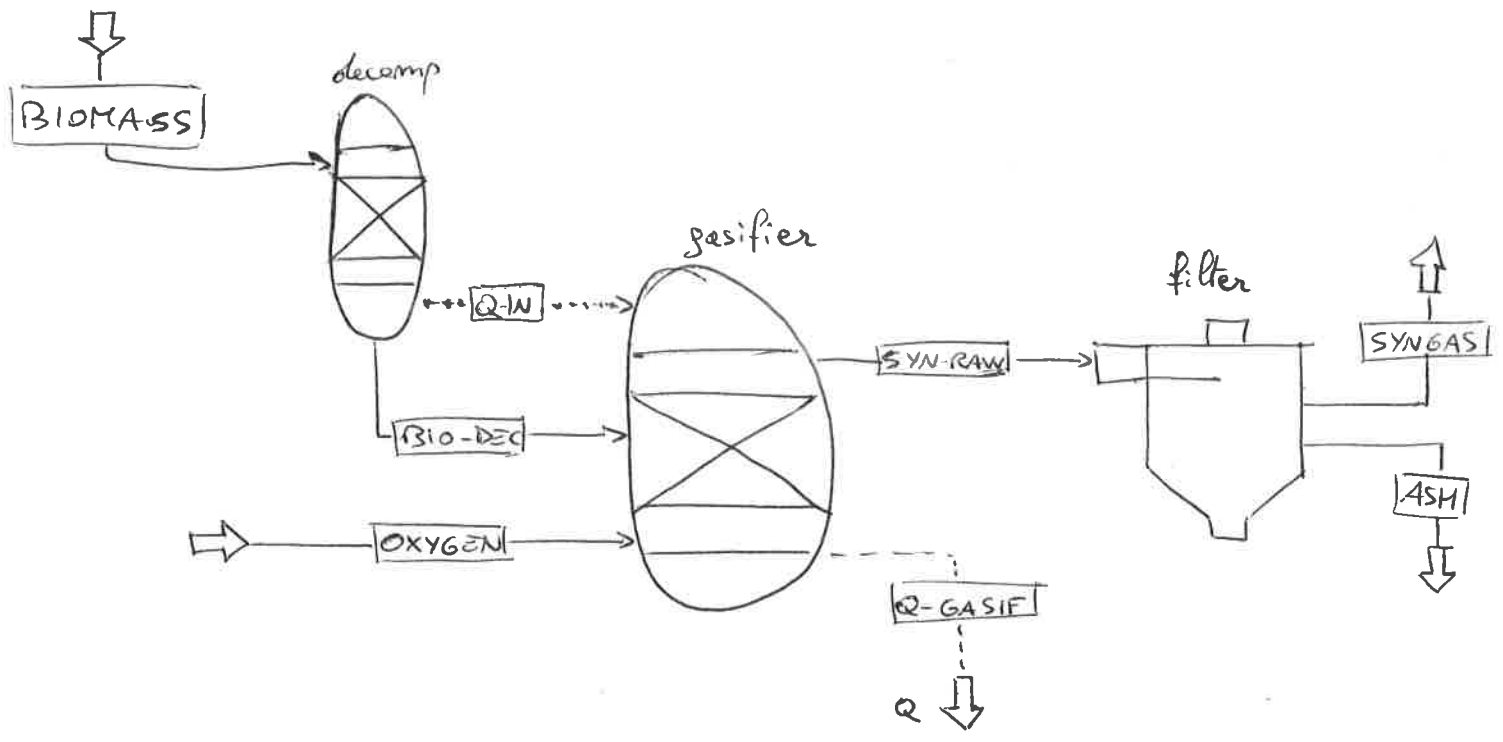
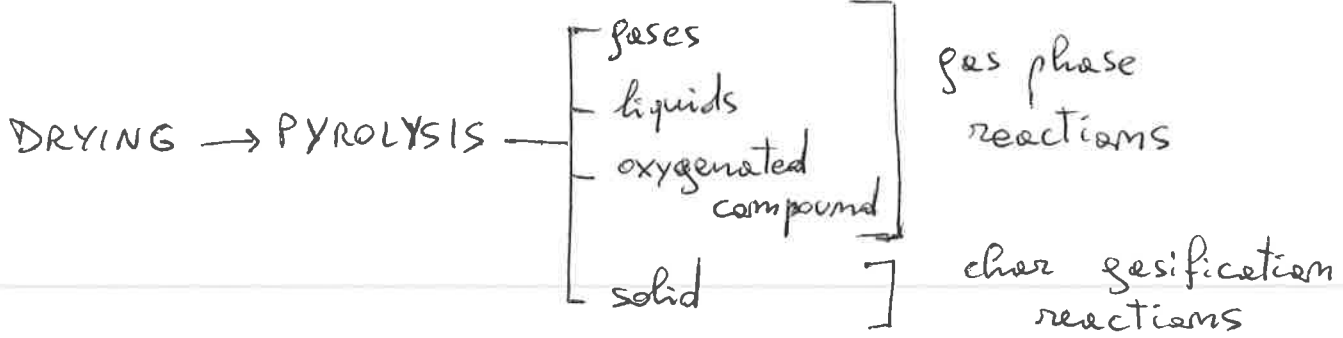
1. Steam reforming $CH_4 + H_2O \rightleftharpoons CO + 3H_2$ $\Delta H^\circ = 206 \frac{kJ}{kmol}$
 endothermic reaction \rightarrow CH_4 conversion favoured at high temperature
2. water gas shift $CO + H_2O \rightleftharpoons CO_2 + H_2$ $\Delta H^\circ = -41 \frac{kJ}{kmol}$
 exothermic reaction \rightarrow CO conversion favoured at low temperature but kinetics disadvantaged

⚠ The methane reaction requires a catalyst to be activated. Indeed, the sp^3 hybridization of carbon makes the C-H bonds of CH_4 very strong.

⚠ Since the WGS reaction is exothermic, the shifter usually consists of adiabatic reactors at different temperatures. This allows to exploit both thermodynamics and kinetics. Catalysts are also used here.



GASIFIER for Gasification. It consists of the thermochemical decomposition of carbonaceous material into fuel gas rich in CO and H₂, called syngas. ~~The procedure~~ The process occurs in air-deficient conditions and by the addition of air or another gasification agent.

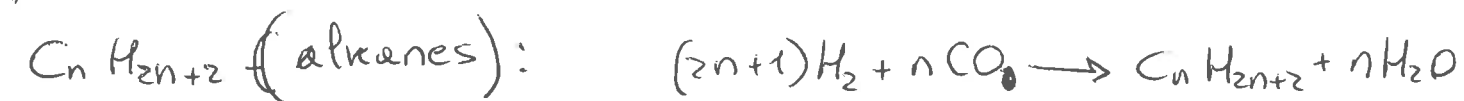


FOCUS: Fischer-Tropsch process (wikipedia)

It's a collection of chemical reactions that converts a mixture of CO and H₂. These reactions occur in the presence of metal catalysts, typically at temperatures of 150-300 °C and pressures of one to several tens of atmospheres. The process was first developed by ~~Franz Fischer~~ Fischer and Tropsch (1825).

F-T process is an important reaction in both coal liquefaction and gas to liquids technology for producing liquid hydrocarbons. In the usual implementation, CO and H₂, the feedstocks for FT, are produced from coal, natural gas, or biomass in a process known as gasification. It then converts these gases into a synthetic lubrication oil and synthetic fuel.

The F-T process involves a series of chemical reactions that produce a variety of hydrocarbons, ideally having the formula



The formation of methane (CH₄) is unwanted. Most of the alkanes produced tend to be straight-chain, suitable as diesel fuel. In addition to alkane formation, competing reactions give small amounts of alkenes, as well as alcohols and other oxygenated hydrocarbons.

Converting a mixture of H₂ and CO into aliphatic products is a multi-step reaction with several ~~and~~ intermediate compounds.

The growth of the hydrocarbon chain may be visualized as involving a repeated sequence in which hydrogen atoms are added to carbon and oxygen, the C-O bond is split and a new C-C ~~to~~ bond is formed. For one -CH₂- group produced

By $CO + 2H_2 \rightarrow (CH_2) + H_2O$, several reactions are necessary:

- Associative ~~adsorb~~ adsorption of CO
- Splitting of the C-O bond

- Dissociative adsorption of $2H_2$
- Transfer of $2H$ to the oxygen to yield H_2O
- Desorption of H_2O
- Transfer of $2H$ to the carbon to yield CH_4

The conversion of CO to alkanes involves hydrogenation of CO, the hydrogenolysis of C-O bonds, and the formation of C-C bonds. Such reactions are assumed to proceed via initial formation of surface-bound metal carbenyls. The CO ligand is speculated to undergo dissociation, possibly into oxide and carbide ligands. Other potential intermediates are various C₁ fragments including formyl (CHO), hydroxycarbene (HCHO), hydroxymethyl (CH₂OH), methyl (CH₃), methylene (CH₂), methyldiene (CH), and hydroxymethyldiene (COH). Furthermore, and critical to the production of liquid fuels, are reactions that form C-C bonds, such as migratory insertion. Many related stoichiometric reactions have been simulated on discrete metal clusters, but homogeneous F-T catalysts are poorly developed and of no commercial importance.

③ Focus: Steam explosion [wikipedia]

It is an explosion caused by violent boiling or flashing of water into steam, occurring when water is ~~either~~ either superheated, rapidly heated by fine hot debris produced within it, or heated by the interaction of molten metals (as in a fuel-coolant interaction, or FCI, of molten nuclear-reaction fuel rods with water in a nuclear reactor core following a core meltdown) - Pressure vessels, such as pressurized water (nuclear) reactors, that operate ~~at~~ above atmospheric ~~conditions~~ pressure can also provide the conditions for a steam explosion - The water changes ~~es~~ from a liquid to a gas with extreme speed, increasing dramatically in volume - A steam explosion sprays steam and boiling-hot water and the hot medium that heated it in all directions ~~if not otherwise contained~~, creating a danger of scalding and burning -

Steam explosions are not normally chemical explosions, although a number of substances react chemically with steam so that chemical explosions and fires may follow - Some steam explosions appear to be special kinds of boiling liquid expanding vapor explosion, and rely on the release of stored superheat - But many large-scale events, including foundry accidents, show evidence of an energy-release ~~front~~ front propagating through the material, where the forces create fragments and mix the hot phase into the cold volatile one; and the rapid heat transfer at the front sustains the propagation -

If a steam explosion occurs in a confined tank of water due to rapid heating of the water, the pressure wave and rapidly expanding steam can ~~also~~ cause severe water hammer - This was the mechanism that, in Idaho (USA), in 1961, caused the SL-1 nuclear reactor vessel to jump over ~~a~~ 2.7m in the air when it

was destroyed by a criticality accident. In the case of SL-1, the fuel and fuel elements vaporized from instantaneous overheating. Events of this general type are also possible if the fuel and fuel elements of a liquid-cooled nuclear reactor gradually melt. Such explosions are known as fuel-coolant interactions (FCI). In these events the passage of the pressure wave through the predispersed material creates flow forces which further fragment the melt, resulting in rapid heat transfer, and thus sustaining the wave. Much of the physical destruction in the Chernobyl disaster, a graphite-moderated, light-water-cooled RBMK-1000 reactor, is thought to have been due to such a steam explosion.

In a nuclear meltdown, the most severe outcome of a steam explosion is early containment building failure. Two possibilities are the ejection at high pressure of molten fuel into the containment, causing rapid heating; or an in-vessel steam explosion causing ejection of a missile into, and through, the containment. Less dramatic but still significant is that the molten mass of fuel and ~~reactor~~ reactor core melts through the floor of the reactor building and reaches ground water; a steam explosion might occur, but the debris would probably be contained, and would in fact, being dispersed, probably be more easily cooled.

③ FOCUS: Chemical potential [wikipedia]

In thermodynamics, chemical potential of a species is energy that can be absorbed or released due to a change of the particle number of the given species, in a chemical reaction or phase transition. The chemical potential of a species in a mixture is defined as the rate of change of a free energy of a thermodynamic system with respect to the change in the number of atoms or molecules of the species that are added to the system. Thus, it is the partial derivative of the free energy with respect to the amount of the species, all other species' concentrations in the mixture remaining constant. The molar chemical potential is also known as partial molar free energy. When both temperature and pressure are held constant, chemical potential is the partial molar Gibbs free energy. At chemical equilibrium or in phase equilibrium the total sum of the product of chemical potentials and stoichiometric coefficients is zero, as the free energy is at a minimum.

FOCUS: Gibbs free energy [wikipedia]

In thermodynamics, the Gibbs free energy is a thermodynamic potential that can be used to calculate the maximum of reversible work that may be performed by a thermodynamic system at a constant temperature and pressure. The Gibbs free energy is the maximum amount of non-expansion work that can be extracted from a thermodynamically closed system (one that can exchange heat and work with its surroundings, but not matter); this maximum can be attained only in a completely reversible process. When a system transforms reversibly from an initial state to a final state, the decrease in Gibbs free energy equals the work done by the system to its surroundings, minus the work of the pressure forces.

The Gibbs energy is also the thermodynamic potential that is minimized when a system reaches chemical equilibrium at constant pressure and temperature. Its derivative with respect to the reaction coordinate of the system vanishes at the equilibrium point. As such, a reduction in G is a necessary condition for the spontaneity of processes at constant pressure and temperature.

close system

THERMODYNAMIC POTENTIALS	TEMPERATURE ENTROPY (THERMAL nat. variab.)	PRESSURE VOLUME (MECHANICAL nat. variab.)
internal energy dU	$T \cdot ds$	$- P \cdot dV$
enthalpy dH	$T \cdot ds$	$+ V \cdot dP$
Helmoltz free energy dF	$- S \cdot dT$	$- P \cdot dV$
Gilbs free energy dG	$- S \cdot dT$	$+ V \cdot dP$

open system

$$\left[\begin{aligned} dU &= T \cdot dS - P \cdot dV + \sum_i \mu_i dn_i \\ dH &= T \cdot dS + V \cdot dP + \sum_i \mu_i dn_i \\ dF &= -S dT - P \cdot dV + \sum_i \mu_i dn_i \\ dG &= -S dT + V \cdot dP + \sum_i \mu_i dn_i \end{aligned} \right.$$

CHEMICAL POTENTIALS

↙
evolution of molar numbers for each element.

MAXWELL RELATIONS

They are a set of equations which are derivable from the symmetry of second derivatives and from the definitions of the thermodynamic potentials. The structure is a statement of equality among the second derivatives for continuous functions. It follows directly from the fact that the order of differentiation of an analytic function of two variables is irrelevant.

SCHWARZ' THEOREM

with

$x_i, x_j =$ natural variables for that potential (n)

$$\frac{\partial}{\partial x_j} \left(\frac{\partial \phi}{\partial x_i} \right) = \frac{\partial}{\partial x_i} \left(\frac{\partial \phi}{\partial x_j} \right)$$

It is seen that for every thermodynamic potential there are $n(n-1)/2$ possible Maxwell relations.

The four most common Maxwell relations are the equalities of the second derivatives of each of the four thermodynamic potentials, with respect to their thermal natural variable (T, S) and their mechanical natural variables (P, V):

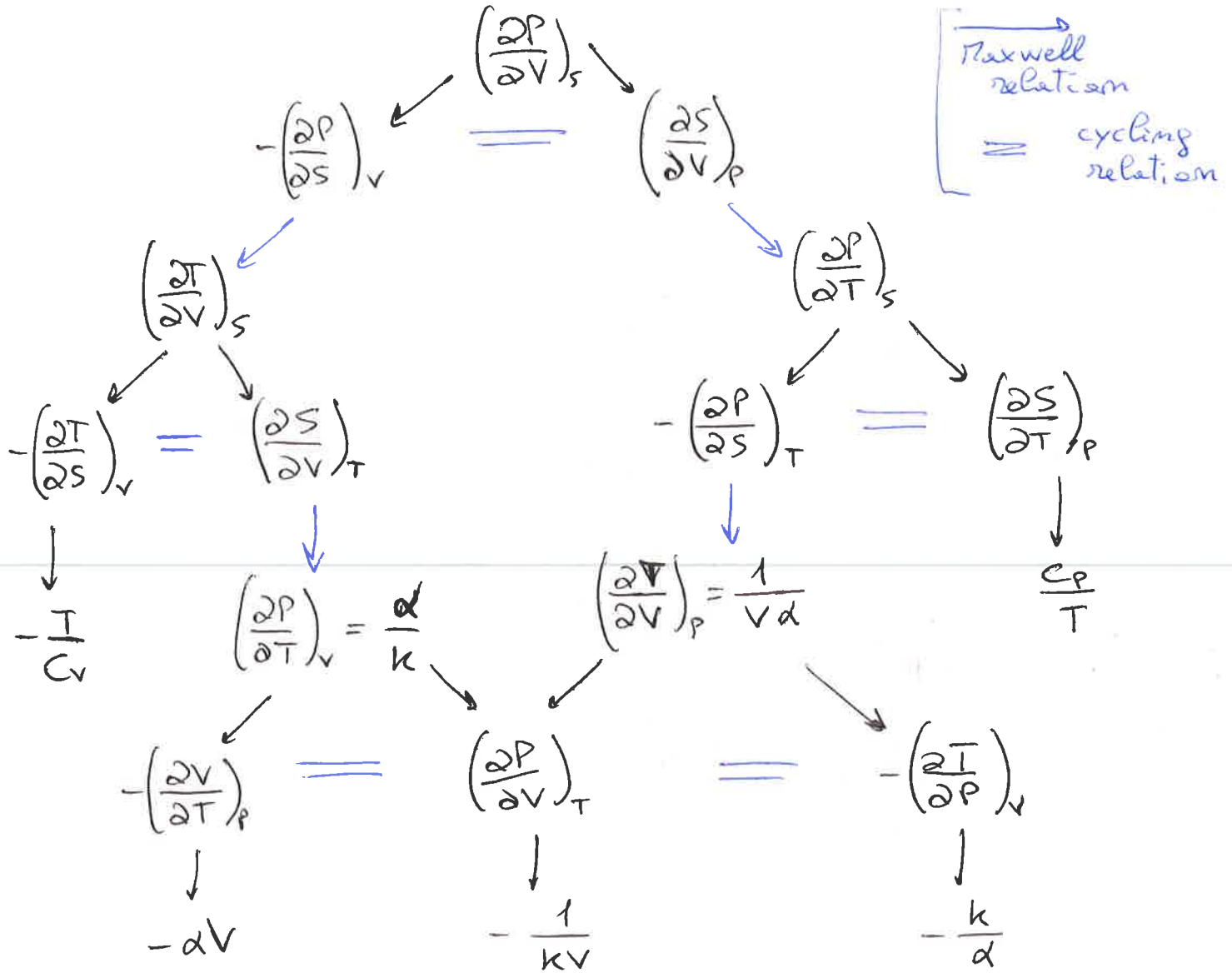
$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V = \frac{\partial^2 U}{\partial S \partial V} \quad \rightsquigarrow \quad U = f(S, V)$$

$$\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P = \frac{\partial^2 H}{\partial S \partial P} \quad \rightsquigarrow \quad H = f(S, P)$$

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V = - \frac{\partial^2 F}{\partial T \partial V} \quad \rightsquigarrow \quad F = f(T, V)$$

$$- \left(\frac{\partial S}{\partial P} \right)_T = \left(\frac{\partial V}{\partial T} \right)_P = \frac{\partial^2 G}{\partial T \partial P} \quad \rightsquigarrow \quad G = f(T, P)$$

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad \text{coeff. of thermal expansion} \quad ; \quad \kappa = - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad \text{compressibility}$$



DERIVATION

$dU = T dS - P dV$

$$\begin{cases} T = \left(\frac{\partial U}{\partial S}\right)_V, & \text{with } -P dV = 0 \\ -P = \left(\frac{\partial U}{\partial V}\right)_S, & \text{with } T dS = 0 \end{cases}$$
 First derivatives

second derivatives $\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S}\right)_V = \frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V}\right)_S$

therefore $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$ Maxwell equation

$dF = -S dT - P dV$

$$\begin{cases} \left(\frac{\partial F}{\partial T}\right)_V = -S, & \text{with } -P dV = 0 \\ \left(\frac{\partial F}{\partial V}\right)_T = -P, & \text{with } -S dT = 0 \end{cases}$$
 I deriv.

$\frac{\partial}{\partial V} \left(\frac{\partial F}{\partial T}\right) = \frac{\partial}{\partial T} \left(\frac{\partial F}{\partial V}\right)$ II deriv.

therefore $-\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V$ Helmholtz equation

$$dH = T dS + V dP$$

$$\begin{cases} \left(\frac{\partial H}{\partial S}\right)_P = T, & \text{with } V dP = 0 \\ \left(\frac{\partial H}{\partial P}\right)_S = V, & \text{with } T dS = 0 \end{cases} \quad \begin{array}{l} \text{I} \\ \text{deriv.} \end{array}$$

$$\frac{\partial}{\partial P} \left(\frac{\partial H}{\partial S}\right) = \frac{\partial}{\partial S} \left(\frac{\partial H}{\partial P}\right) \quad \text{II deriv.}$$

$$\text{therefore } \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad \text{Enthalpy equation}$$

$$dG = V dP - S dT$$

$$\begin{cases} \left(\frac{\partial G}{\partial P}\right)_T = V, & \text{with } -S dT = 0 \\ \left(\frac{\partial G}{\partial T}\right)_P = -S, & \text{with } V dP = 0 \end{cases} \quad \begin{array}{l} \text{I} \\ \text{deriv.} \end{array}$$

$$\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial P}\right) = \frac{\partial}{\partial P} \left(\frac{\partial G}{\partial T}\right) \quad \text{II deriv.}$$

$$\text{therefore } \left(\frac{\partial V}{\partial T}\right)_P = - \left(\frac{\partial S}{\partial P}\right)_T \quad \text{Gibbs equation}$$

③ FOCUS: How is Biogas produced? (Gasum)

Biogas is produced through the processing of various types of organic waste. It is a renewable and environmentally friendly fuel made from 100% local feedstock that is suitable for a diversity of uses including road vehicle fuel and industrial uses. The circular-economy impact of Biogas production is further enhanced by the organic nutrients recovered in the production process. Biogas can be produced from a vast variety of raw materials (feedstocks). The biggest role in the Biogas production process is played by microbes feeding on the biomass.

Digestion carried out by these microorganisms creates methane, which can be used as it is locally or upgraded to Biogas equivalent to natural gas quality, enabling the transport of the Biogas over longer distances. Material containing organic nutrients is also produced in the process, and this can be utilized for purposes such as agriculture.

STAGES IN BIOGAS PRODUCTION

Biogas is produced using well-established technology in a process involving several stages:

1. Biowaste is crushed into smaller pieces and slurried to prepare it for ~~the~~ the anaerobic digestion process. Slurrying means adding liquid to the biowaste to make it easier to process.
2. Microbes need warm conditions, so the biowaste is heated to around 37°C .
3. The actual Biogas production takes place through anaerobic digestion in large tanks for about three weeks.

4. In the final stage, the gas is ready for use by enterprises and consumers, for example in a liquefied form or following injection into the gas pipeline network.

TURNING DIVERSE RANGE OF MATERIALS INTO GAS

Biogas production starts ~~from~~ from the arrival of feedstocks at the biogas plant. A diverse range of solid as well as sludge-like feedstocks can be used.

Materials suitable for biogas production include:

- biodegradable waste from enterprises and industrial facilities, such as surplus lactose from the production of lactose-free dairy products;
- spoiled food from shops;
- biowaste generated by consumers;
- sludge from wastewater treatment plants;
- manure and field biomass from agriculture.

The material is typically delivered to the biogas plant's reception pit by lorry or waste management vehicle.

A delivery of solid matter such as biowaste will next undergo crushing to make its consistency as even as possible. At this point, water containing nutrients obtained from a further stage in the production process is also mixed with the feedstock to take the rate of solid matter down to only around one-tenth of the total volume.

This is also when any unwanted non-biodegradable waste, such as packaging plastic or out-of-date food waste from shops, is separated from the mixture. This waste

④ is taken ~~the~~ to a waste treatment facility where it is used to generate heat and electricity. Biomass that has passed through slurrification is combined with biomass delivered in the form of slurry to the biogas plant and pumped into the pre-digester ~~the~~ Tank where enzymes secreted by bacteria break down the biomass into an even finer consistency.

Next, the biomass is sanitized before entering the actual biogas reactor (digester). In sanitization, any harmful bacteria found in the material are eliminated by heating the mixture to above 70°C for one hour. Once sanitized, the mass is pumped into the main reactor where biogas ~~production~~ production takes place. Sanitization makes it possible to use the fertilizer product in agriculture.

BIOMASS IS TURNED INTO GAS BY MICROBES

In the biogas reactor, microbial action begins and the biomass enters a gradual process of fermentation.

In practice this means that microbes feed on the organic matter, such as proteins, carbohydrates and lipids, and their digestion turns these into methane and carbon dioxide.

Most of the organic matter is broken down into biogas - a mixture of methane and carbon dioxide - in approximately three weeks. The biogas is collected in a spherical gas holder from the top of the biogas reactors.

~~Digestate~~ DIGESTATE UTILIZED AS FERTILIZERS OR GARDENING SOIL
The residual solids and liquids created in biogas production are referred to as digestate. This digestate goes into a post-digester reactor and from there further into storage tanks. Digestates are well suited for uses such as fertilization of fields.

Digestate can also be ~~digestated~~ centrifuged to separate the solid and liquid parts.

Solid digestates have uses such as fertilizers in agriculture or in landscaping and can also be turned into gardening soil through a process of maturation involving composting.

Digestates are centrifuged to yield enough process water for the sterilification of biowaste at the beginning of the process. This helps reduce the use of clean water.

The centrifuged liquid is rich in nutrients, particularly nitrogen, that can be separated further using methods such as stripping technology and used as fertilizers or nutrient sources in industrial processes.

CLEAN BIOGAS HELPS MOVE TOWARDS LOW-CARBON SOCIETY

Gas would already be ready for several uses straight from the biogas plant gas holder. However, before being injected into the gas pipeline network or used to fuel vehicles, it will still undergo purification.

In this upgrading process, gas is filtered and flows into

⑤ columns where it is scrubbed by cascading water at a very specific pressure and temperature. Water efficiently absorbs carbon dioxide and sulfur compounds contained by the gas. Biogas can also be purified using other methods, such as passing it through activated carbon filters to remove impurities.

The final upgraded biogas injected into the gas network is at least 95% and usually around 98% methane.

Upgraded biogas still contains a couple of per cent of carbon dioxide as its further separation from methane is not cost-effective let alone sensible as regards the usability of the gas. Biogas is dried carefully before injection into the gas network to prevent condensation in winter subzero conditions.

The biogas produced can be used for purpose such as fuelling municipal waste management vehicles, urban buses or private cars. At the same time, gas ~~use~~ serves as evidence of those practical actions that are taking us towards the low-carbon society of the future.

FOCUS: Anaerobic digestion (wikipedia)

A collection of process by which microorganisms break down biodegradable material in the absence of oxygen. The digestion process begins with bacterial hydrolysis of the input materials. Insoluble organic polymers, such as carbohydrates, are broken down to soluble derivatives that become available for other bacteria. Acidogenic bacteria then convert the sugars and amino acids into carbon dioxide, hydrogen, ammonia, and organic acids. These bacteria convert these resulting organic acids into acetic acids, along with additional ammonia, and carbon dioxide. Finally, methanogens convert these products to methane and carbon dioxide. Anaerobic digestion is used as part of the process to treat biodegradable waste and sewage sludge. As part of an integrated waste management system, anaerobic digestion reduces the emission of landfill gas into the atmosphere. A.D. ~~is widely~~ ~~used~~ can also be fed with purpose-grown energy crops, such as maize. A.D. is widely used as a source of renewable energy. ~~Anaerobic digestion~~ is The process produces a biogas, consisting of methane, carbon dioxide, and traces of other "contaminant" gases. This biogas can be used directly as fuel, in combined heat and power gas engines or upgraded to natural gas-quality biomethane. The nutrient-rich digestate also produced can be used as fertilizer.

• PROCESS

Many microorganisms affect A.D., including acetic acid-forming bacteria and methane-forming archaea. These organisms promote a number of chemical processes in converting the biomass to biogas. Anaerobes utilize electron acceptors from sources other than oxygen gas. These acceptors can be the organic material itself or may be supplied by inorganic oxides from within the input material. When the oxygen source in an anaerobic system is derived from the organic material itself, the

⑥ "intermediate end products are primarily alcohols, aldehydes, and organic acids, plus carbon dioxide. In the presence of specialised methanogens, the intermediates ~~that~~ are converted to the "final" end products of methane, carbon dioxide, and trace levels of hydrogen sulfide. In an anaerobic system, the majority of the chemical energy contained within the starting material is released by methanogenic bacteria as methane.

- 1) **HYDROLYSIS**: in most cases, biomass is made up of large organic polymers. For the bacteria in anaerobic digesters to access the energy potential of the material, these chains must first be broken down into their smaller constituent parts. These constituent parts, or monomers, are readily available to other bacteria. The process of breaking these chains and dissolving the smaller molecules into ~~the~~ solution is called hydrolysis. Through this molecules are broken down into simple sugars, amino acids, and fatty acids.
- 2) **ACIDOGENESIS**: it results in further breakdown of the remaining components by acidogenic bacteria. Here, VFAs are created, along with ammonia, CO_2 , H_2S , as well as other byproducts.
- 3) **ACETOGENESIS**: ~~Here~~, simple molecules created through the acidogenesis phase are further digested by acetogens to produce largely acetic acid, as well as CO_2 and H_2 .
- 4) **METHANOGENESIS**: here, methanogens use the intermediate products of the preceding stages and convert them into CH_4 , CO_2 , and H_2O . These components make up the majority of the biogas emitted from the system. Methanogenesis is sensitive to both high and low pHs and occurs between pH 6.5-8.

The remaining, indigestible material the microbes cannot use and any ~~the~~ dead bacterial remains constitute the digestate.

+ CONFIGURATION

More initial build money and a larger volume of the batch digester is needed to handle the same amount of waste as a continuous process digester. Higher heat energy is demanded in a thermophilic system compared to a mesophilic system and can also be known as dry digestion.

A.D. can be performed as a batch process or continuous process. In a batch system, biomass is added to the reactor at the start of the process. The reactor is then sealed for the duration of the process. In its simplest form batch processing needs inoculation with already processed material to start the anaerobic digestion. In a typical scenario, biogas production will be formed with a normal distribution pattern over time. A more advanced type of batch approach has limited the ~~other~~ odour issues by integrating anaerobic digestion with in-vessel composting. As the batch digestion is simple and requires less equipment and lower levels of design work, it is typically a cheaper form of digestion. In continuous digestion processes, organic matter is constantly added or added in stages to the reactor. A single or multiple digesters in sequence may be used.

The two conventional operational temperature levels for anaerobic digesters determine the species of methanogens ~~in~~ in the digesters: Mesophilic ($30 \div 38^\circ\text{C}$) or Thermophilic ($43 \div 57^\circ\text{C}$). In typical scenarios, three different operational parameters are associated with the solids content of the feedstock to the digesters: High solids (dry), high solids (wet), low solids (wet).

⑦ Digestion systems can be configured with different levels of complexity: in a single-stage digestion system, all of the biological reactions occur within a single, sealed reactor or holding tank; in a two-stage digestion system, different digestion vessels are optimised to bring maximum control over the bacterial communities living within the digesters.

Under typical circumstances, hydrolysis, ~~and~~ acetogenesis, and acidogenesis occur ~~what~~ within the first reaction vessel. The organic material is then heated to the required operational temperature prior to being pumped into a methanogenic reactor.

The residence time in a digester varies with the amount and type of feed material, and with the configuration of the digestion system. In a typical two-stage mesophilic digestion, residence time varies between 15 and 40 days, while for a single-stage thermophilic digestion, residence times is normally faster and takes around 14 days.

The A.D. can be inhibited by several compounds, affecting one or more of the bacterial groups responsible for the different organic matter degradation steps. The degree of the inhibition depends, among other factors, on the concentration of the inhibitor in the digester.

TARS AND CHAR FROM THE PYROLYSIS OF COALS (Fynes et al.)

The yields of the ~~product~~ TAR from Abernethy anthracite was insufficient for detailed chemical analysis. The hydrogen distributions in the Tar are summarized with micrographs of the coals and selected chars, are reproduced.

• TAR YIELDS: in every test, ~~the~~ the tar yields exceeded those obtained in the Gray-King assay. The main reason was that the test were performed under dynamic conditions, whereas in the G-K assay there is no flow of carrier gas and the pyrolysis vapours coke more readily on the hot gas and silica surface, with a consequent reduction of Tar yield. A marked increase ~~in~~ in the yield of tar was ~~observed~~ observed on increasing the H_2 pressure from 0.1 to 30 MPa. The tar yield from the bituminous coal increased from 18 to 40% and that from the brown coal from 22 to 32%w, indicating the increase in stabilization by H_2 of the free radicals formed during pyrolytic fragmentation of the coal structures. This trend was not apparent for pyrolysis in N_2 . The product yields from the experiment with 0.1 MPa of H_2 closely resembled those obtained in N_2 .

• CHEMICAL COMPOSITION: ultimate analysis showed that the tars produced in H_2 had lower H_2 contents than those produced in N_2 and that the H_2 content decreased ~~and~~ and C/H ratio increased. Increasing the N_2 pressure had no significant effect on either the H_2 content or the C/H ratio of the tars. Increasing the H_2 pressure reduced the oxygen content of the tars, whereas increased N_2 pressure did not. The oxygen appeared as water rather than carbon oxides, and the absence of significant concentrations of carbon oxides in the gaseous products. Ionizable proton concentrations were significantly reduced as the H_2 pressure increased, but not when the N_2 pressure was increased.

⑧ Gas chromatographic analysis of the tar solutions indicated the presence of naphthalene and higher aromatic hydrocarbons.

- NMR ANALYSES: The NMR data on the tars from the bituminous and brown coals show that as the hydrogen pressure increased, so did the proportion of H₂ atoms in aromatic environments. Accompanying this increase was a decrease in the percentage of H₂ atoms in aliphatic side chains. The increase in aromaticity of the tars may be due to cyclization of side chains followed by aromatization of the naphthenic ring or by pyrolytic fragmentation of the side chain to form the parent aromatic compound. Previous work on tar characterization and the increased gas yields due to increased free radical stabilization at the higher pressures suggest the pyrolytic fragmentation would be the favoured route.

- INFRA-RED ANALYSES: Infra-red analyses of the bituminous coal tars gave spectra typical of low-temperature tars although there were differences ~~of~~ on ~~whether~~ whether H₂ and N₂ was used. The N₂ tars were similar to each other in all important respects. They all showed prominent phenolic OH bands at ≈ 3300 and 1250 cm^{-1} ; the ratio of the absorbances due to aliphatic CH at 2920 cm^{-1} and aromatic CH at 3060 cm^{-1} was high, suggesting ~~multi~~ aromatic ring multisub-solutions (at 810 and 750 cm^{-1}). They are di- and tri-substitutions, were of similar absorbance in all the tars produced in N₂. The spectrum of the 0.1 MPa H₂ ~~tar~~ tar ~~from~~ from the bituminous coal was similar to that of the tars produced in N₂, whereas the tars produced in H₂ at 5 and 30 MPa were markedly more aromatic, with stronger absorption bands at 3060 cm^{-1} .

• COAL AND CHAR

CHEMICAL COMPOSITION: The maceral analyses of the coals show that the three coals were rich in vitrinite and relatively low in ash (4-5.5%). Proximate analyses of the chars

show that an appreciable proportion of the volatile matter was retained after pyrolysis. The H_2 contents of all 18 chars were remarkably similar, within the range 3-3.5%. The oxygen contents fell at the higher hydrogen pressures but remained constant in N_2 .

CONCLUSIONS

Liquid and gaseous yields from the pyrolysis of the three coals at 575°C in H_2 were higher than those in N_2 and increased with increasing H_2 pressure but not with increasing N_2 pressure.

All the tar yields ~~were~~ were in excess of those obtained in the G-K assay, and the gas yields were lower, except from the anthracite and the bituminous coal in 30 MPa H_2 .

H_2 ceases to have a significant protective influence on the rapid pyrolysis of coal at low pressures. The yields and compositions of the tars from the 0.1 MPa H_2 experiments were similar to those obtained by pyrolysis in N_2 .

The tars produced in H_2 at 5 and 30 MPa were considerably more aromatic than under other conditions; this increase in aromaticity is due to loss of H_2 -rich sidechains.

The anthracite and brown coal ~~exhibited~~ exhibited ~~no~~ caking tendencies on pyrolysis at 575°C ~~and~~ only under 30 MPa H_2 , when extensive fusion occurred and coherent chars were formed. The bituminous coal fused readily under all conditions although in 30 MPa N_2 , particle expansion was restricted by the high pressure.

③ FOCUS: Chemical reactor (Wikipedia)

is an enclosed volume in which a chemical reaction takes place. In chemical engineering, it is generally understood to be a process vessel used to carry out a chemical reaction. Chemical engineers design reactors to maximize net present value ~~for~~ for the given reaction. Designers ensure that the reaction proceeds with the highest efficiency towards the desired output product, producing the highest yield of product while requiring the least amount of money to purchase and operate. Energy changes can come in the form of heating or cooling, pumping to increase pressure, frictional pressure loss or agitation.

The most common basic types of chemical reactors are tanks and pipes or tubes. Both types can be used as continuous reactors, and either may accommodate one or more solids, but the reagents and products are typically fluids. Reactors in continuous processes are typically run at steady-state, whereas reactors in batch processes are necessarily opened in a transient state. When a reactor is brought into operation, either for the first time or after a shutdown, it is in transient state, and key process variables change with time.

There are three idealised models used to estimate the most important process variables of different chemical reactors:

- Batch reactor model (DSTR),
- Continuous stirred-tank reactor model (CSTR),
- Plug flow reactor model (PFR).

Key process variables include:

- residence time; - volume; - temperature;
- pressure; - concentrations; - heat transfer coeff.

Chemical ~~reactions~~ reactions occurring in a reactor may be exothermic, meaning giving off heat, or endothermic, meaning absorbing heat. A tank reactor may have a cooling or heating jacket or cooling or heating coils wrapped around the outside of its vessel wall to cool down or heat up the contents, while tubular reactors can be designed like heat exchangers if the reaction is strongly exothermic, or like furnaces if the reaction is strongly endothermic.

FOCUS: Technology Description [biouhli.com]

BIOMASS PREPARATION: This procedure involves removal of mechanical impurities, crushing, homogenisation and soaking of the biomass.

HTC PROCESS: Soaked biomass is pumped into the HTC reactor, where it is pressurised to 25 bar by means of steam and heated up to 225°C; once the catalyst is added the process of biomass composition, dehydration and carbonisation will be commenced. Mass with pasty consistency is the output from the HTC process.

MECHANICAL DEHYDRATION: Mechanical compression is applied in order to remove 50% of the water from the cooled-down coal paste. This part of the process ~~produces~~ produces coal cake. Larger part of the separated water is re-used in the production process.

DRYING: Using the waste heat from the HTC process the coal cake is ~~dry~~ dried to the moisture content required by the customer, usually 5-25%. Drying process ~~produces~~ produces pulverised biocoal.

PELLETISATION: Based on the customer requirements the ~~based~~ pulverised biocoal can be pressed into requested shape and dimensions.

FOCUS: Hydrothermal Carbonization

[wikipedia]

HTC is a chemical process of conversion of organic compounds to structured carbons. It can be used to make a wide variety of monostructured carbons, simple production of brown coal substitute, SYN gas, liquid petroleum precursors and humus from biomass ~~the~~ with release of energy.

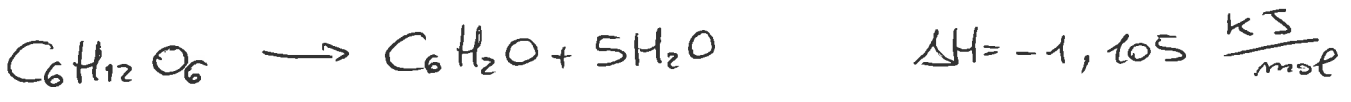
The ~~pro~~ carbon efficiency of most processes to convert organic matter to fuel is relatively low.

alcoholic fermentation	→	67%
gasification to H ₂ or CH ₄	→	60%
gasification and F-T synthesis	→	50%
wood charcoal production	→	30%
production of humus	→	5-10%

In poorly designed systems the unused carbon escapes into the atmosphere as CO₂, or when fermented as CH₄. Both gases are considered to be climate-damaging. In addition, heat is ~~related~~ released in these processes, which is not general_{ly} used. ~~Advanced~~

PROCESS

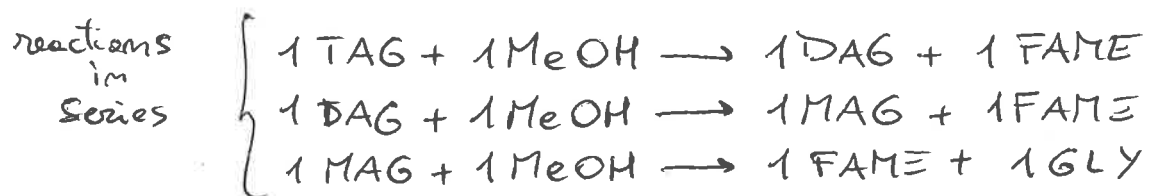
Biomass is heated together with water to 180°C in a pressure vessel, in particular vegetable material, simplified as sugar with the formula C₆H₁₂O₆. The pressure rises to about 1MPa (10bar). During the reaction, H₃O⁺ are also formed which reduce the pH to 5 and lower. This step can be accelerated by adding a small amount of citric acid. In this case, at low pH values, more carbon passes into the aqueous phase. The effluent reaction is exothermic, that is, energy is released. After 12 hours, the carbon of the reactants is completely reacted. The equation is:



EFFICIENCY

As a result of the exothermic reaction of HTC, about $\frac{3}{8}$ of the calorific value of the biomass based on the dry mass is released. If the process is managed properly, it is possible to use this waste ~~from~~ heat from wet biomass to produce dry biocoal and to use some of the converted energy for energy generation. In a large scale technical implementation of hydrothermal carbonization of sewage sludge, it has been shown that about 20% of the fuel energy content contained in 80% end-dried HTC coal is required to heat the process. Furthermore, approximately 5% of the generated energy content is necessary for electrical operation of the plant. It has ~~provides~~ proved particularly beneficial in the case of the HTC process that, with mechanical dehydration, more than 60% of the dry substance content can be achieved in the raw carbon, and thus the energy and equipment expenditure for the final drying in the coal is low compared to conventional drying methods of these slurries.

BIODIESEL MOLECULE \rightarrow FAME



TAG = triglyceride DAG = diglyceride MAG = monoglyceride

MeOH = methanol GLY = glycerol

FAME = fatty acid methyl esters