Thermochemical Energy Processes

What is a Biomass?

Biomass is a material with an organic matter. It is from animals, vegetables or human activities. Some examples of feedstock are oil and sugar from crops, animal wastes and municipal solid wastes.

Biomass is assessed by the proximate and the ultimate analysis: the first one is about the external composition and it can determine the amount of three phases through volatile matter (gaseous phase), fixed carbon (solid phase) and moisture (liquid phase); also it determines HHV (energy) and ash content. This analysis is due to TGA technique, where biomass is heated and the weight is reduced. The second analysis determines internal composition, therefore it explains elements which form the biomass: it can determine the percentages of carbon, hydrogen, oxygen and other elements.

What kinds of conversion are there?

Biomass is used through different processes, but after it is treated with the adequate conversions. They can be physical, chemical or biochemical, and thermal. We speak about physical conversion for treatment of physical composition, dimension, color, size and molecular characteristics.

Steam explosion is a pretreatment about physical size of biomass, which can reduce the feedstock (usually wood) through a quickly depressurization. The aim of this process is to brake long fiber chain and help the cellulose digestion.

The chemical conversions are about molecular composition and chemical reactions, such as Fisher-Tropsch reaction with SNG conversion process. While the biochemical conversions are about organic matter, through bacteria and carbon percentage, such as fermentation or anaerobic digestion.

Finally, the thermal conversion is about reactions due to thermic conditions, such as combustion or higher energy process.

How is a reaction assessed about energy?

The elements of a reaction are characterized with an energy value; it is called Heating Value and can be Higher (HHV) or Lower (LHV). It is referred at water phase: if water is gaseous we use LHV, instead if water is liquid we use HHV.

Generally, heating value is the difference between standard condition and reaction condition for each component. Therefore, energy of reaction is calculate through Enthalpy. It is standard when it is referring on singular element on standard condition, while enthalpy of reaction is the difference between the sum of enthalpies of products and the sum of enthalpies of reactants. This means that it is possible to determine enthalpy of combustion too, for a combustion reaction. Thermodynamics teaches that if enthalpy of reaction is negative, reaction is exothermic, so it produces heat; if enthalpy of reaction is positive, reaction is endothermic, so it needs of heat.

What is kinetics?

The microscopic element of a reaction is analyzed through kinetic laws. They determine the evolution of a reaction, studying the speed and the order of composition changing. Thanks to kinetic constant, the

evolution of composition for each element is assessed. Moreover, engineers can provide to use of the catalysts with the reducing of energy of activation, without chemical composition variations.

In general, two kinds of system are described: for closed system reaction rate is about the variation of composition on time; while for open system reaction rate is about the amount of input and output of moles. Therefore this is right for Continuous or Discontinuous Stirred Tank Reactor.

On Plug Flow Reactor, the term about variation of composition is absent and the reaction rate is calculate only with the amount of inlet and outlet through the pipe.

Then, direct and indirect reactions are distinguished and the different between both systems is the reaction rate of all reaction. Both system are described by the kinetic constants and the composition product, with respectively order number. Reaction rate is zero in equilibrium state, therefore relation between direct and indirect system is calculated.

There are four parameters which can describe the composition evolution in the reaction: conversion about the element A, yield about the element P in function of limiting element A, selectivity is the relation between both yield on conversion, and differential selectivity is the relation between reaction rates of P and A.

What is thermodynamics?

The macroscopic elements of a reaction is analyzed through thermodynamic laws. They determine the energy on the reaction, through Peng-Robinson relation for fluidized elements in supercritical conditions. Also Maxwell relations can describe thermodynamics of a system by the first and second thermodynamic laws: energy is the difference between heat and work evolution, and entropy is the heat variation in a specific temperature. Therefore, Maxwell relations are about three terms: the first is the energy specification, such as enthalpy, Gibbs free energy, Helmotz free energy and internal energy; the second is about thermic conditions with the variation of temperature or entropy; the third is about mechanic conditions with the variation of volume or pressure.

For open system, chemical potential is important to calculate because it describes the molar phase evolution. To assess the equilibrium state, Gibbs free energy must be minimized, therefore variation of temperature and pressure are negligible and the sum of chemical potential is zero. This is the main element for non-stoichiometric approach, without composition definition and through specific software. The stoichiometric approach is due to equilibrium constant calculated by the relation between the composition of products and the composition of reactants.

An important definition for the composition account is the phases rule. This help to calculate step, after the main parameters definition. Principally, it defines the degrees of freedom, different for number of phases and number of components. A diagram of pressure and temperature can help the element accounting.

Is for real system the same assessment?

For real system many parameters have to be considered, therefore new considerations are given. When the chemical potential are analytically calculated, pressure term in logarithmic argument becomes fugacity (or activity for liquid phase). This term contains the coefficient of fugacity that changes partial

pressure of a percentage with the variation of temperature. This means that fugacity accounting is very difficult for a real system and, sometimes, it is negligible.

Which kinds of Reactor exist?

Reactors are used in different situation and they are classified in function of use, of dimension, of work and of number of phases. A reactor can be built for laboratory, for pilot or for industrial use; also can work with homogeneous or heterogeneous phases; finally it can be discontinuous or continuous.

All kind of reactor are described through three main ideal reactors:

The Discontinuous Stirred Tank Reactor (DSTR) is a closed system with the hypothesis of well mixing for the evolution of reaction. Because of the instantaneous reaction, the design parameter is time, that is calculate with and integral formula of reaction rate and degree of advancing, with the density of mixed product.

The Continuous Stirred Tank Reactor (CSTR) is an open system with the same hypothesis of DSTR of well mixing and instantaneous reaction, but in this case there is an inlet and outlet assessment. Therefore design parameter changes and becomes volume. The tank volume is calculated with a linear function of relation between degree of advancing and reaction rate, after weight measuring. This means that volume is fixed due to general parameters and boundary conditions.

The Plug Flow Reactor (PFR) is a pipe system with an inlet and an outlet defined, and the hypothesis of homogeneous sections, without axial diffusion. Similar boundary conditions are about CSTR because of open system, but there is a little difference: the tank volume is the design parameter too, but there is a non-linear function for its calculation. The volume is defined through the integer function of relation between degree of advancing and reaction rate, with the weight.

Now, a matching between CSTR and PFR is possible to assess optimal condition. The calculation of volumes give a constant value for the first type and an exponential growth for second type. Volume is the amount area under the line, so the best design is PFR or a series of many CSTR.

What is P&ID meaning?

Piping and instrumentation design is the planning of general design of a complete system. It describes how component flows work and where some monitoring and control tools are fixed.

There are some conventional rules to be understandable for everyone, such as continuous or dotted lines, and circular symbols with specific letters. P&ID is used to define the scheme of equipment, piping, instruments and utilities.

In P&ID scheme is not defined the safety. It is the third level for security in a process system, after control and personal protection. Safety is about worker and people, it uses pipelines and valves which monitor temperature and pressure. Other tools are used to avoid dangerous situations, such as chips burner and connection of security, particularly used on combustion system, with high temperature and depressurized tanks.

What is a combustion reaction?

When an element reacts with oxygen, at high temperature, a combustion occurs with the main formation of water and carbon dioxide molecules. Speaking about biomass combustion, the products are just water and carbon dioxide, also char amount for solid phase.

A system with combustion stage has got a heating storage system for using and transformation of produced energy. Each combustion system is with some conversion systems, and tools of transformation are used in function at kind of phase of materials. In fact, for solid elements steam turbines are designed, while for liquid elements internal combustion engines are performed, and for gaseous elements fuel cells are used.

In general, combustion systems are used in co-generation heating and power (CHP) process. Therefore, there is an energy production from biomass burning. In particular, turbines are used to power generation, heat exchangers are used to heat generation.

Finally, pyrolysis is a process like combustion, but without oxygen. This is due to the absence of air inlet with steam of feedstock. A pyrolysis reaction is generated by very high temperature conditions, with much production of char or carbonization materials.

What is an anaerobic digestion?

An important biochemical conversion is anaerobic digestion. It is the process of methane production from biomass treatment through bacteria use. The main characteristic of anaerobic digestion is the absence of air and the poorly of oxygen. All process is composed by three steps: hydrolysis, acidogenesis and methanogenesis.

Before all process a steam explosion is necessary to help bacteria in digestion of cellulose. Therefore, first stage is the hydrolysis of sugar, fats and protein, so the formation of long chain fatty acids (LCFA), amino acids, glucose and xylose. The quantity of each element is due to percentage of nitrogen, acidity and fat ratio in the feedstock.

The second stage is the acidogenesis, so there is a formation of acids with the reduction of long chains. In fact, volatile fatty acids (VFA) formation occurs from LCFA for 30% of component. Other products are acetic acids, carbon dioxide and hydrogen molecules, respectively for 50% and 20% of feedstock. This is depending from acidity and difference between amino acids and others composition.

Last stage is the production of methane, due to two different ways called methanogenesis n.1 from acetic acids and methanogenesis n.2 from gaseous ratio. Both ways are balanced for respectively 70% and 30% of production due to the right environment of anaerobic digestion.

All the process of digestion is very delicate. It is very important to respect some parameters about environment, such as temperature, acidity, nutrition and toxic elements, dry matter and carbon – nitrogen fraction. For instance, the temperature determines what kind of bacteria works, thermophiles, mesophiles or psycophiles. It is necessary to have a neutral pH and the correct amount of organic matter in the feedstock. In the same time, nitrogen is an essential parameter to avoid the inhibition of the system, because too much nitrogen ratio brakes the digestion process. Finally, toxic elements could be heavy metals or inorganic components which unhelp bacteria digestion.

The final aim of the anaerobic digestion is the biogas production. It is used for energy stream in environmentally friendly systems. When a biogas is burned much heat is produced by the combustion system, without the dangerous gases releasing on air.

What is a gasification process?

A gasification is a gas production process through four steps. Usually a system have a gasification zone near a combustion zone because the process needs of heat energy. With biomass use, synthetic natural gases (SNG) are produced, such as hydrogen and carbon monoxide.

The first step is the drying of feedstock (usually wood) with a production of steam and dried wood. The temperature is about 150 degrees because evaporation of moisture is very important.

The second step is the pyrolysis with very high temperature (700 degrees). This is the cause of water absence and the importance of complete drying before. Wood pyrolysis produces gases products and charcoal.

Sometimes oxidation step occurs for charcoal transformation in smokygas, with higher temperature than pyrolysis.

In the last step, reduction process transforms all product in final gas called syngas.

Recently there are some improving at gasification systems, such as the Gussing plant with FICFB technology. This means that the system uses a Fast Internal Circulating Fluidized Bed, so there both gasification and combustion zones are linked by energy and bed material exchanging.

On last years, Gussing plan has improved the system with a generation of SNG and FT gases in the same time, through the cleaning produced gas.

The most important assessment is the BOD or COD for biomass composition. They determine the oxygen demand for the right environment conditions. They are measured with the relation between milligrams of oxygen on liters of water.

How is biodiesel produced?

The biodiesel molecule is produced through several steps from fatty acid chain. The whole process is called transesterification, because is the transformation of triglyceride molecules with methanol, or ethanol, in fatty acid methyl esters (or fatty acid ethyl esters).

In details, transesterification is composed by three different steps: the triglyceride is decomposed in di- and mono- glyceride with methanol; each products reacts with methanol to produce three FAME and glycerol molecule. FAME molecule is the biodiesel, while glycerol is the product not used in this process, but with a great energy potential.

All the process occurs through four steps: a pretreatment process is necessary before the hydrolysis with enzymes to fats digestion; then fermentation occurs with nutrients of digestion and distillation can storage the produced fuel.