# 3 Background and technical basis for the proposed E-M-F-System

There are many ways to enhance the efficiency of bio-energy production, for example by using: recent discoveries of more effective enzymes and bacteria, creating more ideal circumstances for the process, adapting the latest technologies, and better usage of by-products and products. As mentioned in the last units, the combination of several of these biological processes seems to be a promising and efficient utilization of biomass. In this chapter, technical analysis of the E-M-F-System is based on the suitable technology of each single process as well as the relationship between them. This ensures that the technological demand of every process in the system is being considered as a part of a whole in order to create a coherent and efficient system.

In the whole life cycle of this system, there are lots of perspectives to be considered, e.g. raw materials – types of crops, planting, harvesting, and transportation; pre-treatment technologies, production, selling and use of the products – the whole cycle of energy production and utilization. But the key point of this thesis is the process of combining these biological processes. Therefore, technological analysis of the combination is the main task of this paper. It is taken as the key research point of this work. Thus, the basic technology of every process and a combination assessment is undertaken for each potential process with promising technologies further explained.

# 3.1 Bio-ethanol production

Bio-ethanol production is the basis of the E-M-F-System. Production methods, production flow and development influence the further combination possibilities within this system. In the following sections, the basis of bio-ethanol production, its definition, methods and development are explained.

# 3.1.1 Background and definition of bio-ethanol production technology

Bio-ethanol is destined to become a major substitute for compounds of fossil fuels used in transportation. In some applications and locations it is already widely in use. The key advantage of bio-ethanol is that today's cars can use it in gasoline blends without expensive retooling of their original Otto engines. In addition, bio-ethanol can be delivered using the existing fuel infrastructure without extensive modification [18].

Bio-ethanol and bio-ethanol/gasoline blends have a long history as alternative transportation fuels. According to the statistics of International Energy Agency, the transportation sector accounts for about 60 % of the world's total oil consumption, corresponding to 27.3 % of the total energy use in the world [63]. Bio-ethanol was used in Germany and France as early as 1894 in the incipient

industry of internal combustion (IC) engines. Brazil has utilized bio-ethanol as a transportation fuel since 1925. The use of bio-ethanol for fuel has been wide-spread in Europe and the United States since the early 1900s [2, 63].

Before 1975, about 80 % of crude oil was imported from remote areas in Brazil. The demand for ethanol depends on the price of original materials, ethanol and fossil fuel, and on the other hand, also the technical development of the automobile. In Brazil, in 1931, there was already a 5 % (by volume) ethanol mixture rate (E5) with the traditional oil for cars. Then with design developments the mixture rate was raised up to E25 (25 % ethanol mixture) with a utilization rate of about 72 %. About 19 % of cars currently run with an ethanol mixture rate of 100 % (E100) [2]. Advances in technology and the relatively low price of ethanol versus gasoline are the main reasons why it is predicted that the Brazilian domestic market will reach 28-30 Gl by 2013 and possibly 45-50 Gl by 2030 [10].

In the US, the government has adopted some ethanol friendly policies. For example in 1978, during the competition between ethanol and gasoline, the price of ethanol was only \$0.1/l. Ethanol production in United States, which is primarily derived from corn grain, has more than tripled since 2000. By 2030, ethanol production will be 60 billion gallons and displace 30 % of current petroleum use [2].

World ethanol production for transport fuel tripled between 2000 and 2007 from 17 billion to more than 52 billion liters. From 2007 to 2008, the share of ethanol in global gasoline use increased from 3.7 % to 5.4 %. Worldwide ethanol fuel production reached 22.95 billion U.S. liquid gallons (bg) (86.9 billion liters), with the US as the top producer with 13.2 bg, accounting for 57.5 % of global production. The US together with Brazil accounts for 88 % of the world ethanol production [163]. Largest increases in production volumes is expected in the US, Brazil, the EU, China, India, Indonesia and Malaysia, with the annual global production of bio-ethanol projected to exceed 125 billion liters by 2020, and that of bio-diesel to 12 billion liters [63]. Ethanol production from the first nine biggest ethanol production countries in the world is shown in Figure 3-1.



*Figure 3-1: Distribution of the global ethanol production [163]* 

The basic steps for large scale bio-ethanol production are: biomass pretreatment, sugar fermentation, bio-ethanol distillation, rectification and dehydration. Prior to fermentation, some crops require carbohydrates hydrolysis and saccharification - starch into simple sugars. A typical biomass to bioethanol process is shown in Figure 3-2.



Figure 3-2: A typical bio-ethanol production process

All types of feedstock such as sugar cane, bagasse, miscanthus, sugar beet, sorghum, grain sorghum, switch grass, barley, potatoes, sweet potatoes, cassava, sunflower, fruit, molasses, corn, wheat, straw, cotton, as well as many types of cellulose wastes and harvest can be collected, stored and used for bioethanol production throughout different agricultural seasons. After adding liquefying enzymes, feedstock is disintegrated by using a dispersing machine installed in the mash tub. Thus the starch contained in the feedstock is almost completely released and simultaneously liquefied. Once the grinding is complete, dispersing stops and the mash is cooled to the saccharification temperature (52-55 °C) for about 6 hours.

The fungi or bacteria derived enzymes as well as brewing malt is added in order to guarantee maximum bio-ethanol conversion. Further adjustments (e.g., pH adjusters or disinfectants) are hardly needed and thereby are not to be considered. After saccharification, the mash is cooled, yeast is added, and fermentation proceeds at about 35 °C for at least 44 h. The fermented mash contains 9-18 % of bio-ethanol (volumetrically). For the ethanol to be usable as a fuel, water must be removed. Most of the water is removed by distillation, with a purity of 95-96 %. The water fraction is typically removed in further treatment - ethanol vapor under pressure passing through a bed of molecular sieve beads, containing more than 99 % by weight ethanol. The bead's pores are sized to allow absorption of water while excluding ethanol, assuming to yield anhydrous ethanol. The product is condensed, cooled, stored, and denatured in order to be burned in combination with gasoline in gasoline engines [43].

In order to get a good understanding of the bio-ethanol processes, these processes are categorized into three main blocks – biomass pre-treatment, fermentation process and anhydrous bio-ethanol production process. In every block, mass-, energy- and  $CO_{2-eq.}$  flow is located as a whole entirety. It simplifies the complicated processes of bio-ethanol production, and makes it easy to carry the analysis out. For the most important part – fermentation, some of the latest research suggests that some processes can be also added to or amended, e.g., a combination of simultaneous saccharification and fermentation (SSF), during which the enzyme rates could be maximized by reducing sugar inhibition. This is thought to be the best emendation of the enzymatic conversion of cellulose to ethanol [43]. During these processes, besides the main product of bio-ethanol, some other types of gas is released as a by-product –  $CO_2$  and liquid by-product – stillage come into being simultaneously, all of which will be reused for the following processes. Bio-ethanol production process is shown in Appendix A, while some of the key bio-ethanol production points.

In a typical stillage treatment process, the whole stillage is partially evaporated in a vacuum evaporator. The partially evaporated whole stillage is separated in a decanter centrifuge. The wet grains leave the centrifuge with total solids at about 35 % by weight. The thin stillage from centrifuge is partially recycled as backset, and the remainder is concentrated in evaporator to syrup containing 55 % by weight total solids. To conserve steam and cooling water, the condensation of overhead vapors from the rectifier is accomplished in the evaporator to provide reflux for distillation. The syrup and wet grains are mixed and dried in a gas-fired rotary dryer to produce DDGS. The DDGS leaving the dryer contains 9 % moisture by weight. Makeup water is added only for the cooling tower and the  $CO_2$  scrubber, and no wastewater is produced [43]. Stillage related technologies are summarized in the following sections.

#### **Biomass pre-treatment**

Biomass can be pre-treated by a variety of methods, e.g., by grinding to make the starch available for saccharification and fermentation. Other methods of biomass preparation include that used for starchy material, such as kernels of corn, which is often ground with a ball mill, a roller mill, a hammer mill, or another mill known for grinding vegetable material, and/or other materials for the purposes of particle size reduction. The use of emulsion technology, rotary pulsation, and other means of particle size reduction can be employed to increase the surface area of biomass while raising the effectiveness of flowing the liquefied media. The prepared material can be referred to as being or including "raw starch".

#### Fermentation

Fermentation process is normally operated in a batch, but the process may also be continuous or partially continuous [43]. In a partially continuous fermentation, yeast may be partially recovered from the mash prior to distillation and returned to fermentation. Inoculums of yeast culture often close to 10 % of the fermenter volume is added to the cooled mash and allowed to ferment to completion, usually in less than 2 days [25].

Normally, the use of stillage as back-set is utilized in the course of fermentation. The volume of stillage is reduced by the volume of returned yeast [47], but soluble COD entrained with the yeast increases the COD of the stillage. For every 1 % of residual sugar (based on glucose), a stillage COD increment of 16 g/l can be expected. Therefore, proper control of distillation can greatly affect the COD of stillage. The volume of stillage which results after distillation is inversely proportional to the concentration of ethanol at the end of the fermentation. In a similar manner, when properly used, back-set or stillage recycling (the use of stillage as make-up water for cooking and fermentation) will lower stillage volume [48], but not affect the total amount of COD produced since the stillage strength will be increased by the amount of back-set [49]. An analysis of beet molasses distilleries shows that the use of 30 % back-set reduces stillage production from 15.9 to 12.6 l/l ethanol [50]. The use of backset can reduce consumption of water, steam, and some chemicals, but the accumulation of fermentation product and non-fermentable sugars can inhibit the fermentation process. Therefore, a practical limit of 50 % stillage recycling is considered a maximum [25,44,47,48,51,53]. Above this level of stillage recycling, inhibition of the yeast will lower ethanol yield and increase the COD concentration in the stillage beyond that contributed by the recycled stillage alone [4]. Therefore, efforts to assure high ethanol content of the final mash will reduce stillage volume and improve distillation energy consumption and capacity [44]. Also, ensuring fermentation has reached completion and that residual sugars in the mash are minimized can lower the COD of the resulting stillage.

Several different organisms have been proposed for use in fermenting sugars to ethanol, with different strains of the yeast. Saccharomyces cerevisiae is currently the most widely used due to its robust growth rate and high ethanol tolerance [54]. With proper nutrient and growth conditions, it has been shown that S. cerevisiae can tolerate ethanol concentrations up to 23 % [54]. Since S. cerevisiae ferments lactose poorly, Kluyveromyces marxianus is often employed for the fermentation of whey feedstock [59]. For cellulosic feedstock containing pentose sugars which are not fermentable by S. cerevisiae, the impact of organism selection on stillage COD could be significant since the pentose sugars can amount to 25 % of the feedstock carbohydrates [60, 61]. A significant decrease in stillage COD can be expected from utilizing pentose sugars in the fermentation of cellulosic feedstock, but this has not yet been documented.

For cellulosic feedstock employing enzymatic hydrolysis, saccharification may be aided by the addition of  $\beta$ -glycosidase to the mash to cleave the glucose dimer, cellobiose. Since the activity of  $\beta$ -glycosidase is inhibited by the presence of glucose, the use of saccharification during fermentation, called SSF, is advocated since the fermenting organisms will lower inhibiting glucose concentrations [19, 66]. Also, since higher ethanol yields have been achieved using SSF, the resulting stillage should have a lower organic content. A simple modification to SSF which is shown to be effective is periodic application of ultrasound to the fermentation to enhance enzyme contact with the substrate [4, 67].

The bacterium Zymomonas mobilis has been shown to produce higher ethanol yields due to a lower cell yield, but its lower ethanol tolerance and lower feed by-product return has limited its widespread application [57]. Difficulties of separation, lower cell yield, and concern of pathogenic contamination in feed have limited the market for bacterial feed additives. In contrast, yeast is more easily separated, generally accepted as safe in feeds, and has an established market [58]. Genetically engineered Escherichia coli, Zymomo-nas, and yeast with extended substrate capabilities can utilize both 5-carbon and 6-carbon sugars to produce ethanol [24, 62, 65].

There is an interest in the use of thermo-tolerant yeast in thermophilic ethanol production, due to the potential for higher fermentation rates and ethanol yields, and the reduced requirements for cooling [55, 56]. Yet, to date, thermophilic fermenting organisms have suffered from low ethanol tolerance, presumably due to leaky cell membranes at higher temperatures [56].

#### Distillation and dehydration

After fermentation is complete, the ethanol typical  $2\pm 12$  % (by volume) containing mash is pumped to a continuous distillation process where steam is used to heat the mash to its boiling point in the stripper column [25].

The ethanol-enriched vapors pass through a rectifying column and are condensed and removed from the top of the rectifier at around 95 % ethanol. The ethanol-stripped stillage falls to the bottom of the stripper column and is pumped to a stillage tank. With efficient distillation, the stillage should contain less than  $0.1\pm0.2$  % by weight ethanol, but at times when distillation is not optimal, the stillage may contain significant ethanol content. In this case, two molecular sieve beds are placed in parallel with one drying while the other is regenerating. During the regeneration phase a "side stream" of ethanol/water (often around 50 %) is produced, which must be redistilled before it can be returned to the drying process. The "bottoms" from side stream distillation is often blended into the stillage, adding to the stillage volume [4].

Heating of stillage by steam can occur either by direct injection of steam into the bottom of the stripper column or indirectly through a "reboiler" heat exchanger at the bottom of the column [25]. Also true for the cooking process, the direct injection of steam impacts the stillage in two ways. First, the condensed steam adds to the stillage volume and dilutes the contents. In addition, loss of water from the boiler requires the addition of make-up water and increases the blow-down volume from the boiler required to avoid boiler scaling. More boiler feed water use and blow down increases the requirement for boiler chemicals and increases the amount of salts removed in the blow down [68]. Since the blow-down water is normally combined with the stillage, it dilutes the organic content of the stillage and increases the salinity. An analysis of a beet molasses distillery shows that stillage production decreases from 15.9 to 12.7 I/I ethanol when heating is switched from direct steam injection to the use of a re-boiler [50].

In order to allow the blending of ethanol with gasoline, water content must be reduced to less than 1 % by volume. Higher water levels can result in the separation of an ethanol/water mixture below the gasoline phase, which may cause engine malfunction when a fuel tank empties. Unfortunately, separation of ethanol from water by distillation is limited to a purity of around 96 % due to the azeotropic properties of ethanol/water mixtures. The removal of the water beyond the last 5 % is called dehydration or drying. Traditionally, azeotropic distillation is employed to produce higher purity ethanol by adding a third component, such as benzene, cyclohexane or ether, to "break" the azeotrope and produce dry ethanol [69]. To avoid the illegal transfer of ethanol from the industrial market into the potable ethanol market, where it is highly regulated

and taxed, and dry ethanol usually requires the addition of denaturing agents which render it toxic for human consumption, and azeotropic reagents conveniently met this requirement.

Except in the high purity reagent-grade ethanol market, azeotropic drying has been supplanted by molecular sieve drying technology, which is not only more energy efficient but also avoids the occupational hazards associated with the azeotropic chemical admixtures. In molecular sieve drying, ethanol is passed through a bed of synthetic zeolite with uniform pore size which preferentially adsorbs water molecules. After the bed becomes saturated, it must be regenerated by heating or evacuating the bed to drive the adsorbed water. Either liquid or vaporous ethanol can be used, but the dominant and most efficient technology is the vapor-phase "pressure swing" adsorption molecular sieve process [69].

### 3.1.2 Classification and characteristics of basic bio-ethanol production process

Through a comprehensive overview of recent technology in the process of bioethanol production, the production of ethanol from biomass, whether from sugar crops (sugar beets, sugar cane, molasses, etc.), starch crops (corn, wheat, rice, cassava, etc.), dairy products (whey) or from cellulosic materials (crop residues, herbaceous energy crops, bagasse, wood, or MSW) can be basically divided into two generations. The first generation is from sugar and starch crops, and the second is from cellulosic materials. The technology for bioethanol production from the first generation materials is well developed and has been in production in many countries for a long time, such as sugar cane in Brazil, maize in the US, sugar beet and other grains in Europe. The second generation material is still in a research phase for popular and industrial utilization. The deciding factor for bio-ethanol production is the decomposition grade of the crops and the different pre-treatments of the feedstock.

### Pre-treatment - hydrolysis of starch containing feedstock

As stated previously, sugar-based feedstock like sugar cane does not require processing to convert carbohydrates into fermentable sugars. In starch-based feedstock, a mashing and saccharification process is required to produce fermentable sugars [33]. After milling, the starch-based feedstock is introduced into a cooker, with make-up water and  $\alpha$ -amylase, and heated to 90 °C. In this liquefaction process,  $\alpha$ -amylase is employed to cleave long starch polymers to dextran.  $\alpha$ -amylase requires Ca<sup>2+</sup> for activation and has an optimal pH of 6.6. This is generally achieved by the addition of lime as the Ca<sup>2+</sup> source and additional alkali (usually NaOH) as required to reach the optimal pH, since the pH of most grain-mash is below this optimum. After liquefaction, the mash is cooled to below 60 °C and gluco-amylase is added while pH is lowered to the optimal value of 4.5 for this enzyme. The gluco-amylase enzymes attack the ends of dextran and produce fermentable sugars. At this stage, nitrogen and phosphorous nutrients like urea may be added where the nutrient content of feedstock is expected to limit fermentation [4].

### Pre-treatment - hydrolysis of cellulosic feedstock

Hydrolysis of cellulosic feedstock is accomplished through either enzymatic, concentrated acid [34], or dilute acid (usually  $H_2SO_4$ ) hydrolysis, or combinations thereof [9], at elevated temperatures and pressures or specific periods to free the hemicellulose and lignin from the cellulose fibers and to hydrolyze the cellulose to glucose [36].

In enzymatic hydrolysis, extracts of cellulase enzymes obtained from cellulolytic organisms, such as Trichoderma reesei, are added to the feedstock, often along with  $\beta$ -glucosidase, to allow conversion of the cellulose to cellobiose and then to individual glucose units [35]. While enzymatic hydrolysis is considered expensive compared to acid hydrolysis, due to the cost of enzymes and the longer time required (days rather than minutes), it possesses the advantage that side reactions which convert some of the carbohydrates in cellulosic feedstock to non-fermentable sugars are virtually absent [35].

Acid hydrolysis may employ concentrated acids for short periods of exposure or dilute acids for longer periods [37]. A common scheme is to employ a twostage dilute acid hydrolysis, where the hemicellulose is hydrolyzed to xylose and recovered in the first stage and a more vigorous second-stage hydrolysis is employed for conversion of cellulose to glucose [38]. The two streams may be combined or fermented separately [39]. A consequence of acid hydrolysis is the potential loss of glucose to hydroxymethyl furfural and xylose to furfural in side reactions [18]. In combinational hydrolysis processes, dilute acid hydrolysis may be followed by enzymatic treatment to enhance the effect of costly enzyme additions [40]. More complete descriptions of these processes can be found elsewhere [4, 9].

### 3.1.3 Development of the technology

Although in this field, the technology has been greatly improved, there are still challenges that need further investigation. Most research has been done on the hydrolysis of lignocellulose and the use of the by-production for more energy efficiency.

The research of lignocellulose containing materials for bio-ethanol production has been carried out for a long time in the US, Canada, Brazil, and Scandinavian. The key point for this technology is the perversion method that breaks up complicated chains in materials and then breaks the cellulose chains down into C6-sugar like glucose. This is still under research and needs further development [24].

The related micro-organisms comprise of a number of bacteria and fungi with the desirable properties for the process. These micro-organisms can be broadly divided into two groups:

- Native cellulolytic micro-organisms that possess superior saccharolytic capabilities, but do not necessarily result in product formation;
- Recombinant cellulolytic micro-organisms that naturally give high product yields, but into which saccharolytic systems need to be engineered.

For the first step, the development of baker's yeast-saccharomyces cerevisiae is broadly highlighted [8]. Pre-treatment has been viewed as one of the most expensive processing steps in cellulosic biomass to fermentable sugars conversion. Pre-treatment also has great potential for the improvement of efficiency and lowering of cost through development and research.

The other development of bio-ethanol production is to find the other utilizations for the by-products mentioned above. In Chapter 2 - stillage utilization lists the possibility of its use to produce biogas in the process of digestion. The technology of subsequent by-product utilization steps is explicated in the following sections.

# 3.2 Biogas production

Much work has been done and recorded in the reference materials describing biogas which has been generated through digestion from biomass type 1 (residues) and biomass type 2 (energy crops). The technology of biogas production is less difficult than that of bio-ethanol production. Analogically, the species of the raw materials for biogas production are in many ranges, with many kinds of wastes, manure, stillage and energy crops, just as described in Table 2-4.

Biogas typically refers to a gas produced by the biological breakdown of organic matter in the absence of oxygen. It originates from biogenic material and is a type of bio-fuel, which comprises primarily methane and carbon dioxide and may have small amounts of hydrogen sulphide, moisture, oxygen, ammonia and siloxanes as well.

Biogas is produced by the anaerobic digestion of biodegradable materials such as biomass, manure, sewage, municipal waste, green waste, plant material, energy crops and in this study – stillage from bio-ethanol production. If biogas plant is near bio-ethanol plant, transportation cost of raw materials for biogas digestion can be greatly reduced. Besides, stillage from bio-ethanol production is of fine particle size, which needs no extra cutting process of the raw material. It is a fine homogenized media, with no other pre-treatment needed. Biogas could be produced utilizing anaerobic digesters, which are fed with stillage with DM of about 6.8-16.2 % under mesophilic (35-42 °C) or thermophilic (55-65 °C) condition. All of these conditions call for separate species of bacteria. It is thought that mesophilic operations are more safe and stable than thermophilic operations. Some kinds of dilute inoculums or back-up liquid are added during the course of homogenization.

The liquid part produced in the digestion process – digestate can be further treated for the next process. The digestate is separated into solid digestate with a DM of up to 35 % and the liquid digestate. The solid digestate can be further used in the composting process and correspondingly the liquid digestate can be partly used as inoculums with the rest as liquid fertilizer in field.

Biogas production processes can also be divided into three parts: the pretreatment process, the digestion process, and the digestate post treatment process, just as shown in Attachment 2-A. The study of the separation methods and characteristics of the solid and liquid digestate are the key points for the next composting process of solid digestate.

The digestion process proposed here involves anaerobic digestion of the whole stillage in a reactor for a period of 25-30 days or so. The reactor is mixed and held at a mesophilic temperature about 37 °C. The use of mesophilic digestion for stillage is caused by a number of factors, including [4]:

- Lack of availability of thermophilic inoculums
- A perceived higher sensitivity of thermophilic digestion compared with mesophilic digestion
- Concert about restart of intermittently operated thermophilic digesters
- Perceived high organic content in thermophilic effluent compared to mesophilic effluent

Besides, as the whole stillage leaving from the process of distillation is warm at about 102 °C, mesophilic digestion need not use more thermal energy compared to thermophilic digestion. In mesophilic digestion, there is no requirement of parasitic thermal energy under suitable temperature and good inoculation circumstances. Considering DM of the whole stillage with a content of up to 12 %, wet digestion is suitable to be used to produce biogas in the digestion process. With this content, it is allowed for pumping and stirring [105].

Gases such as methane, hydrogen and carbon monoxide (CO) can be combusted or oxidized with oxygen. Biogas produced can be used locally to produce electricity and heat, directly burnt in a boiler, compressed into liquid fuel and mixed with nature gas for autos or transported to a distant area for local use. The heat produced from the use of biogas could be used in biological plants, local heating for houses or industries [116]. Biogas can be used as a fuel in any country for any heating purpose, such as cooking. It can also be used in anaerobic digestion plants where it is typically used in a CHP unit to convert the energy in gas into electricity and heat. The heat can be partly used for the process of digestion and partly for bio-ethanol distillation in the last course. Advanced waste treatment technologies can produce biogas with 55–75 % CH<sub>4</sub>. Biogas can also be cleaned and upgraded to natural gas standards when it becomes bio-methane. After a series of treatments, methane is purified from water,  $CO_2$ ,  $H_2S$ , and other elements. Bio-methane can be mixed with natural gas, compressed and used to power motor vehicles. The produced  $CO_2$  during the process of digestion can be further absorbed and synthesized together with the other  $CO_2$  produced in this system by the biomass during the course of photosynthesis.

For the production of biogas, a mixture of animal manure and energy crops has already brought advantages, with high production of biogas and high  $CH_4$  content in Germany. A typical biogas digestion process in Germany is shown in the following Figure 3-3, which can also be utilized by the digestion of stillage. The figure has been changed a little to reflect the E-M-F-System, with the whole stillage as feedstock, and the digestate used in the next process of composting.



Figure 3-3: Digestion flow sheet of the stillage in E-M-F-System (on the basis of [47])

There is a need for separation process before the whole digestate used in the composting process. Digestate can be separated mechanically in the same manner as animal manure. Separation creates two outputs, a liquid and a fibrous material, which need to be stored and handled separately. It is recommended that the higher dry matter and fibrous fraction should be stored without disturbance, or even composted, in order to avoid any methane emission. Some advantages of digestate separation are that it can [117]:

- produce a stackable dry fraction and pumpable liquid fraction
- lower the volume of liquid requiring storage
- create the potential to export separated fiber and nutrients
- improve efficiency in nitrogen uptake from the liquid
- provide a greater window of opportunity for application of the liquid
- minimize the requirement for mixing of the liquid prior to spreading.

Solid fraction with fibrous fraction can be composted for approximately 60 days and then used as a substitute for chemical fertilizer. The liquid fraction can be re-circulated in the AD process, spread out to the field, or disposed in a sewage treatment plant [105].

There are a number of digestate separation methods. Chemicals can be used to improve separator efficiency and help to partition differential plant nutrients (particularly phosphorus) to the separated fibrous fraction. Separation can also be done by non-mechanical methods, such as sedimentation or filtration through geo-textile tubes. Whatever the method, separators are being used increasingly in biogas plants, connected with either the post-digestion or the main digestion stage. When used in post-digestion, the partitioning of the nutrients between liquid and solid fractions helps the management and efficient redistribution of digestate as a bio-fertilizer [117].

In a comparison between screw press and rotary screen separation of digestate, it is found that the screw press gives higher separation efficiency and is more reliable. The screw press differentially partition more dry matter, volatile solids, carbon, ash and phosphorus to the solid phase than to the liquid phase. Nitrogen, ammonia and potassium are not differentially partitioned between liquid and solid. Decanter centrifuges give good differential partitioning of nutrients, particularly phosphorus, into the separated fibrous fraction. The use of chemicals to coagulate and/or flocculate the liquid prior to centrifuging can improve partitioning [117]. However, decanter centrifuges have high capital and operating costs; as a result, their use tends to be limited to high volume systems such as large pig farms and centralized biogas plants. According to analysis of the different separation methods for the stillage digestate in Chapter 4, it is suggested that centrifugation is the best choice to separate the solid part from liquid part.

# 3.3 Bio-fertilizer production

Compost is a mixture of decayed organic materials decomposed by microorganisms in a warm, moist, and aerobic environment, releasing nutrients into readily available forms for plant to use. The decomposition process originated in China at about 4000 years B.C. [21]. Aerobic composting disposes organic substance (carbohydrate) through micro-organisms with the help of oxygen to change it into  $CO_2$ ,  $H_2O$  and the rest compost. The energy is then freely discharged, through which the heap of the compost is warmed. Humus is then produced. The disposing of glucose during composting is like the following [17]:

 $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + 2.800 \text{ kJ/mol}$ 

Extensive biological stability of the treated waste for low-emission cannot be reached by anaerobic digestion alone, but may be in a combination with additional aerobic post-treatment. One recognized disadvantage of anaerobic digestion is the fact that the solid produced are not typically suitable for direct land application, as they tend to be odorous, too wet and with too high volatile fatty acid (VFA) concentration, which are phyto-toxic. In addition, if the digestate is not performed under thermophilic conditions, the solids are not sanitized. Composting especially for the middle and hard decomposed materials and materials with low water content is considered to be suggestive to be composted. An additional treatment of these solids is required with post composting, providing an appropriate waste management solution [13]. Composting is a key biological process in the circulation of mass and energy in the ecosystem.

The constitution of biomass is different according to input type. Carbohydrates such as sugar, starch, hemi-cellulose are easy to dispose. Lignin is difficult to dispose. Protein can be partially well disposed. Mucin can be disposed very well, while the keratin can be disposed of only with great difficulty. During digestion, lignin and chitin do not decompose, while during composing courses these matters can be well degraded [17].

Most anaerobic fermentation combined with composting is applied to the digestate from dry fermentation. There are some reasons for this: at first, after dry fermentation, there is no need to separate the solid part from liquid part, which can be directly used in the course of composting. Secondly, it is highly needed for the sanitation of digestate, which occurs in mesophilic fermentation at about 37-42 °C. According to the requirement of sanitation of compost, fresh feedstock or digestates collected during anaerobic digestion and during the early stages of aerobic post-treatment are still phytotoxic. For this reason, anaerobic digestate requires final 'polishing' to enhance fertilizer value and applicability as a soil conditioner. Aerobic 'polishing' has been reported as a suitable treatment as it is capable of reducing moisture content, odor along with carbon and pathogens in the digestate thereby enhancing the fertilizer value of organic wastes. The goals of composting are mainly related to these two aspects: hygiene treatment and stability treatment. Composting can be used as not only for odor disposal and soil improvement but also water protection. The utilization of bio-compost meets with the laws of water, fertilizer, solid waste and soil protection. From use of the compost product, the need of composting are listed as to improve the soil structure and quality, reduce the smell, to build humus and to be used as a product in the market. A supply of large amounts of chemical fertilizers causes serious effects on soil and underground water pollution, as only 40 % of applied fertilizer is absorbed by crops, with the rest leaching into the environment [29].

In this system, there are two possibilities. Firstly, digestate can be used directly in the field as a liquid fertilizer, if it is pumpable. Secondly, to separate the digestate into liquid and solid fertilizer, which is convenient to be transported and sold in the market. The solid part prior to discharge, which contains most of the organic content, can also be further disposed in the course of composting. Nutrients contained in organic solid digestate are released more slowly and are stored for a longer time in the soil, thereby ensuring a long residual effect [42]. Improvement of environmental conditions and public health as well as the need to reduce costs of fertilizing crops are important reasons for advocating increased use of organic materials [43]. Application of organic solid digestate also improves the soil microbial properties [44].

It could be suggested that the lack of heat generation during self-heating tests, for anaerobically treated materials, is the result of aerobic micro-organisms having been destroyed during anaerobic treatment periods. However, an increase in electron flow and hydrolysis rate at the onset of post digestion indicates that aerobic micro-organisms survive anaerobic treatment and are active when exposed to oxygen [11]. During anaerobic digestion, there is no requirement of temperature to inactivate pathogen micro-organisms, when anaerobic digestion is followed by a suitable aerobic composting. Aerobic bacteria, actinomycete and fungus can live under the exposure to oxygen [16]. Composting courses can be classified into three groups according to temperature [17]:

- Psychrophilic branch: -4 20 °C bacteria and fungus
- Mesophilic branch: 15 42 °C bacteria and actinomycete
- Thermophilic branch: 45 75 °C bacteria and mesophilic spore

Rice straw, weeds, sugarcane bagasse, corn stalks and stovers, leguminous materials and animal manure can be gathered to form a composting heap. The compost heap can generate heat with a temperature up to 75 °C during intensive composting process due to the activities of bacteria, fungi, and other micro-organisms. Most of the organic substance decomposes during this process. If it is necessary, a post composting process can create a better, more stable bio-fertilizer product. The post composting process takes a long time, requiring 3-4 months before the warm wastes are fully decomposed and ready for use as bio-fertilizer. The big rough compost can be cut into fine particles in order to be stored and sold as products. Compost can be classified into different categories according to the quality and use of the compost. According to German solid waste management (BIOAbfV), for a good hygiene composting, a temperature above 55 °C must be maintained for at least 2 weeks, or above 65 °C, it must be more than a week [20].

Besides, for optimal aerobic composting, circumstance like trace elements, nitrogen, phosphorus, and calcium must be in the favorable ranges. As the

characteristics of the nutrient substances, the carbon to nitrogen rate (C/N) is set at best between 35:1 and 20:1 in the input stuff of the pile. For example, C/N in the kitchen waste is about 25:1, and after the disposal of composting, the rate is between 15:1 and 20:1. If the rate is too high, the reaction only happens with difficulty and the reaction rate will be slowed down [21]. The favorable pH-value for composting is mostly neutral. During the course of digestion, most of the digestate is in the pH value at around neutral or a little alkaline, which is suitable for use in composting.

During the course of reaction, enough oxygen must be assured. This is different between active and passive ventilation. Especially in the intensive phase, it is normal to use active ventilation. The ventilation rate must be paid attention to, because too much ventilation may make the materials too dry. The structure of the material influences the use of water, the diffusion of air, the colonization space of the micro-organisms, and the speed of disposition. The bio-waste with high content of water can be mixed with other structural materials, like wood chips, branches, etc. Bigger materials can be cut into suitable pieces to get better ventilation. Through rebuilding of the pile, additional fresh oxygen, nutrient substances, and water can be added, and materials can be well mixed to be homogeneous. All kinds of organic materials, which can be used as structure improving subjects: sawdust, straw, rind, branches and other materials, have the following characteristics [21]:

- can be built into the granular structure
- low water content
- degradable, and full of elemental carbon

There are many kinds of biomass, which are suitable as structural materials for use in the course of composting. Normally, these kinds of materials are primarily used on the ground in sty for animal's excrement, feed for animals, remaining in field or burning for heating. In regards to possible storage problems of local structural materials, some garden green wastes and/or municipal wastes can be considered and utilized as well as structural material. In this system, the main composting raw materials are the stillage digestate. To achieve a good ventilation effect, at the bottom of the heap, a platform with aeration appliances or the use of available local structural materials such as the rest stuff like straw peels and root, leaves and stem of the crops can be used as structural materials and mixed together with the stillage digestate. During the first month's intensive composting process, the heap is rebuilt once every one to two weeks to get a good ventilation rate and homogenization. One important factor in the substance for composting process is water content. Water is used for the transportation of nutrient and organic substances for the bacterial in the heap. If there is too high water content, it is not good for the diffusion of air in the heap, and then it will create an anaerobic process. According to the reference, water content in biomass is at best at 55-65 % (weight), and if water content is under 25 % (weight), there will be significant inhibition in the heap [21]. The utilization possibility of composting with these kinds of materials is listed as follows:

• To make full use of rest materials from agriculture.

For example corn husks, straw, leaves and branches of the plants and so on are lacking in water content. Conversely, fine solid stillage digestate is full of water, so it is a good use of these two types of materials to mix them together so as to improve the stability of agriculture wastes, and at the same time amend the quality and structure of soil.

• To produce more fertilizer products.

Solid fertilizer can be used for years and can be sold as product. Liquid fertilizer as there is a lack of enough organic particles after separation can be used as thin liquid fertilizer and directly in the field.

• To make this system circulate more with more sustainability.

The use of composting is the last step of biological disposal of organic substances, through which organic substances can be made more stable and suitable for recycling.

The maturation of compost is also essential. If it is not mature, it can cause a lot of problems, like the decay of the plant root, production of poisonous substances, and the addition of some kinds of heavy metals to the soil. Therefore, the use of composting to achieve suitable compost for the field, and simultaneously a proper composting product is highly needed through the improvement of the composting technology and its market demand. The following situation must be paid attention to during the use of organic fertilizer:

- Situation of the soil
- Height of locally cultivated plants
- Sequences of the crop-planting
- Remaining or exportation of the harvest rests
- Application of organic or mineral fertilizer
- Climate changes (water balance)
- Granulation and structure of the earth
- Development intensity of the earth

When grain stillage is used as a substitute for mineral fertilizer nitrogen, the fertilization costs decrease considerably. Moreover, stillage provides both organic matter and basic nutrients (i.e. mainly potassium and phosphate), which can be a feasible approach to improving the emission balance in the cycle of bio-ethanol without worsening the energy balance [18]. Aerobic composting of solid wastes from fermentation when followed by land application for biomass can recover the nutrients contained in organic compost.

## 3.4 Conclusion of the technologies for this system

The technologies of bio-ethanol, biogas and bio-fertilizer production have been already developed and are already in use. The combination of some of these technologies is still under research and needs to be utilized further. Although, there are still many problems that still need to be worked. Through the study of these technologies in this system above, the following conclusions can be made:

#### 3.4.1 Full combination of these three processes

In this Chapter, the basic characteristics of these three biological treatments are illustrated, and the relationship between them is introduced and explained as well. There is no technological obstruction between these processes. Thus, it can be feasible to utilize this system to produce bio-energies.

When considering the technology of bio-ethanol production and the characteristics of the stillage, stillage can also be used directly in the next process through a temporary storage tank as buffer. The suitable biogas digestion process is the continuous, mesophilic, one stage and wet digestion. Other digestion technologies like two-stage process, thermophilic or batch could be used by stillage as well, but are less efficient, thus are not suggested in this study.

In this E-M-F-System, the digestate is further used to produce a final product – fertilizer - as has been shown to be feasible in the above technological analysis. There must be a process of separation before it is processed in the composting. Separation efficiency is related to the water content left in the solid digestate, and is an important parameter for the composting technology. Otherwise, due to the small particle size of the solid stillage digestate, structural materials are needed for a better composting effect. Due to this consideration, practical considerations such as the availability of local structural materials must be ensured, so that the composting process can be further carried out.

Based on current energy and environmental issues, an energy production system should produce as much energy as possible, and make full use of the raw materials and rest materials. After the production of bio-ethanol, the rest stillage is used for biogas digestion, and further the solid part of the digestate can be used in the course of composting. All the CO<sub>2</sub> produced during these processes together with the liquid and solid fertilizer can be absorbed and reused by biomass, through which a new circulation can be brought out.

#### 3.4.2 Problems of theoretical analysis

Bio-energy already provides the majority of renewable energy worldwide and is considered to have the potential to provide a large fraction of world energy demand over the next century. At the same time, if biomass systems are managed properly, bio-energy will contribute to meet the requirement of reducing carbon dioxide emissions and environmental protection.

Through the overview of these three biological technological processes, it is possible to combine them to support a biological system. But the concept of this system lacks of a lot of support or there may be some obstacles:

It is a novel application of the technologies in the E-M-F-System to produce energy instead of using the stillage as feedstock for animals. The question comes up: is it energy efficient to use stillage for the further energy production?

The efficiency of biogas production from stillage is still in doubt. In order to answer this question, further experiments or pilot tests need to be carried out before it is put into industrial utilization.

The use of stillage in this system requires two additional biological processes. If it is too difficult to implement it for users, it may not be viable. Thus, in the following chapters, these questions are addressed and analyzed sequentially.

# 4 Laboratory research

The idea for this research originated in how to improve the current process for bio-ethanol production, particularly the use of its by-product, combining a series of biological processes to achieve an ecologically sustainable outcome and to promote a high-efficiency energy production system, the E-M-F-System. Currently the most often globally used input materials for bio-ethanol production are starch and sugar containing crops, for example, in Germany, the main materials are energy crops such as wheat, triticale, rye, barley, maize and sugar beet.

This proposed system has not yet been exactly described in any published work nor has significant research been done on the topic. Thus, there is a lack of reliable analysis of how stillage can used in the course of digestion to produce energy, and furthermore, how to make full use of the rest materials, to reduce the production of wastes, and to get a better compost product. Research on stillage digestate as compost is lacking. This hampers the utilization of stillage for energy production. Therefore, it is imperative to conduct laboratory research in order to support the concept of this system.

In the prior summary of the references in other studies, some research related to the stillage used to produce biogas has already been done in the laboratory. In order to extend these existing studies, the objective of this research is to answer the following questions:

- Is the E-M-F-System technologically possible and feasible?
- Are the materials between each process suitable?
- What are the characteristics of the materials between each process?
- What is the energy potential of these materials?
- Is the system energy efficient?

To a practical extent, the attempt is made to assess the roles of feedstock, byproduct recovery, biogas yield, composting potential and sustainability. The key parameters concerning this research are listed as follows:

- Process stability
- Biogas yield
- Bio-degradation rate of organic matter
- Energy potential changes
- The production of an environmentally safe bio-fertilizer.

This research is carried out in two parts: first, an experiment using digestion to produce biogas, with stillage as the raw material, and the second part using the rest material from digestion – digestate to produce quality compost. At the end of this chapter conclusions are made about the E-M-F-System based on the laboratory experiments.