

# From biomass-rich residues into fuels and green chemicals via gasification and catalytic synthesis

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## Abstract

Recycling carbon present in residual streams enhances sustainability and creates local wealth.

Enerkem Inc. is a leading biomass gasification company headquartered in Montreal, Québec. The approach Enerkem has been developing involves: identification of low cost residual streams as feedstock, sorting, biotreatment (anaerobic and/or aerobic) and preparation of an ultimate residue (RDF). The latter is a rather uniform material that can be fed, as a fluff, to a bubbling bed gasifier in a staged gasification to carry out, sequentially, the needed chemical reactions that result in high syngas yields. Process can be adjusted to reach desired gas composition for synthesis or electricity generation as well as gas conditioning to produce an ultraclean syngas. Products for such a process are:

- i) syngas with an appropriate range of H<sub>2</sub>/CO ratios,
- ii) CO<sub>2</sub> (which is recovered),
- iii) solid char as a residue composed of the inorganic fraction of the raw material and some unconverted carbon that “coats” the inorganic matrices, and
- iv) water that needs to be treated to meet the sewage specifications and thus be sent into the water distribution system of a given municipality.

Enerkem is developing two parallel valorisation routes; a) heat and power and b) synthesis of (bio)methanol as a high yield product. The methanol is the platform intermediate that can be turned into ethanol (also with high yields), and other green chemicals. Yields of ethanol as the end product are above 350



liters/tonne of feedstock (dry basis) to the gasifier. Residual heat, also a product of the process, is used in the process itself and, as well, for district heating. The combined work of the Industrial Chair in Cellulosic Ethanol at the Université de Sherbrooke, focused on fundamentals in parallel and close relationship with Enerkem that focused in technology development and implementation. The company has moved from bench scale, to pilot (150 kg/h in Sherbrooke, Québec), to demo (1500 kg/h in Westbury, Québec) to commercial implementation (12 500 kg/h in Edmonton, Alberta). Economics of the process are favourable at the above commercial capacity given the modular construction of the plant, reasonable operational costs and a tipping fee provided by the municipality for the conversion of the ultimate residue. When the project is in “production mode” Edmonton will have achieved 90% diversion of the urban waste from landfills and, furthermore the reduction in GHG (CO<sub>2</sub> equivalent) will be of 80% taking as reference the use of fossil fuel derived gasoline to yield the same energy output as the ethanol obtained by the ‘Enerkem approach’.

*Keywords: alcohols synthesis, syngas production, methanol, ethanol, heterogeneous catalysis, gasification.*

## 1 Introduction

Enerkem is a technology developer specialised in the gasification platform: feedstock preparation, feeding systems, syngas production, syngas clean-up, catalytic reforming and catalytic synthesis. Enerkem’s technologies has been tested in the conversion of various waste products such as municipal solid waste, non-recyclable commingled plastics, residual biomass (from forest and agricultural operations) and numerous others carbonaceous residual streams to produce syngas, which is then used for the production of heat and/or power or for catalytic synthesis of biofuel (methanol and ethanol) and others specialty chemicals.

Biomass-derived ethanol plays an important role in reducing petroleum dependency and providing environmental benefits, through its role as fuel additive in the transportation fuel market. Ethanol is a winter fuel oxygenates and also an octane enhancer. For this reasons the Canadian government has legislated an objective of 5% of ethanol in gasoline for 2012. Aiming at this objective Enerkem’s technology is an alternative to produce ethanol from non-food feed. At the same time is an alternative to landfill and incineration.

This paper focuses on characteristics of the syngas produced by gasification of RDF and on the catalytic synthesis of alcohols as second generation of biofuels.

## 2 Gasification of biomass

### 2.1 The basics

Gasification is the terminology used to describe the conversion of the organic matter present in wastes and residues into a synthetic gas, a mixture of H<sub>2</sub>, CO,



CO<sub>2</sub>, and low molecular weight hydrocarbons of formula C<sub>x</sub>H<sub>y</sub>. The gasifier is the vessel where the conversion is carried out.

The following chemical reactions are predominant during gasification:

- 1 Thermal decomposition (i.e. pyrolysis), which covers dehydration as well as cracking reactions leading to gases, intermediate vapours and carbon structures known as “char”;
- 2 Partial oxidation of the “char” which forms CO and CO<sub>2</sub> generating heat for the otherwise endothermic reactions;
- 3 Steam-carbon, i.e. the water-gas reaction, that converts carbon structures into H<sub>2</sub> and CO;
- 4 Steam reforming of intermediates formed by thermal decomposition;
- 5 Reactions involving CO<sub>2</sub> and H<sub>2</sub> with carbon and with intermediates. Such reactions are kinetically slower than the steam induced reactions at the conditions used in gasifiers;
- 6 Water gas shift reactions that lead to a desired H<sub>2</sub>/CO ratio.

The different gasification strategies and corresponding processes diverge on how to manage the six groups of chemical reactions stated above and how to generate and provide heat for the endothermic reactions.

Since thermal decomposition requires activation and, more important, the steam-carbon and steam-reforming reactions, as well as those with CO<sub>2</sub> are endothermic, heat has to be provided for gasification to proceed within reasonable reaction times (preferably seconds) to limit the size of vessels. Heat can be provided either indirectly (via steam, produced in a steam generation unit, or via the recirculation of a hot carrier, heated in a separate interconnected vessel) or directly (via air or oxygen injection). In the latter procedure heat is produced by oxidation of i) chemical species or functionalities present in the feedstock itself, ii) intermediates (“tar” and “char”, the latter is also known as “pyrolytic carbon”, formed by thermal decomposition, and/or iii) primary gaseous products. Since the amount of O<sub>2</sub> needed to satisfy thermal needs is below that needed for complete oxidation (i.e. combustion) of the feedstock, the net result can be considered, stoichiometrically, as a partial oxidation of the feedstock.

Reaction conditions: reactants concentrations, partial pressures, temperature, turbulence and reaction time are of paramount importance in defining the yields and product distribution from thermal gasification. The following “rules” are of the essence:

1. When the process is conducted at low temperatures (<750 °C) and short reaction times (of the order of seconds or even fractions of a second) thermal decomposition will predominantly produce oligomeric intermediates. The latter, will not be able, kinetically (low T and short t), to undergo subsequent secondary cracking or react with steam. Upon condensation of the oligomeric intermediates, the latter becomes the “primary tar”. In such situation, the rate processes are those characteristic of low temperature fast pyrolysis which is



known to produce large amounts of primary tar. The latter has a chemical structure derived from the constitutive macromolecules of the feedstock. In primary tar from biomass, oligomeric anhydrosugars and lignin-derived oligomers are predominant.

2. At higher process temperatures ( $>750\text{ }^{\circ}\text{C}$ ), the cracking of the intermediates produces high concentrations of free radicals whose recombination competes, kinetically, with steam (and  $\text{CO}_2$ ) reforming reactions. When recombination reactions are predominant, the formation of large amounts of “secondary tar” is observed. Such secondary tar is of aromatic nature and it is often accompanied by soot, formed at high severities.

3. Uncatalyzed carbon-steam and carbon- $\text{CO}_2$  reactions are not kinetically significant, below  $800\text{ }^{\circ}\text{C}$ . For this reason, activated carbon production, using steam, is carried out at  $>800\text{ }^{\circ}\text{C}$ . The presence of alkali catalyzes such reactions. This is important in biomass gasification since alkali (K being the most significant) is present in all biomasses. The point is that steam-carbon reactions can take place in a convenient temperature range when the reaction chemistry can be controlled by the presence of alkali. The choice of strong or weak alkali decides on the range and concentration (partial pressure) of steam to be used.

Reactor configuration and associated fluid-dynamics, which are characteristic of each gasifier type, are also of paramount importance in gasification since they are responsible for heat and mass transfer rates and, as well, they define the residence time distribution patterns. Coupling effectively fluid-dynamics with reaction kinetics (which as previously discussed depend on temperature, pressure, concentration of reactants and reaction time) is the key to high yields and desired product selectivity.

## 2.2 The technology

The process commercialized by ENERKEM<sup>TM</sup> Inc., is the result of efforts started in the early 80's that led to the development of a core technology which couples fluid bed reactors with advanced gas conditioning strategies to provide a clean synthetic gas. The latter can be used for the co-generation of electricity and/or process heat. When combined cycles are used the electrical energy efficiency significantly exceeds that of the combustion/steam cycle. When the technology is coupled, in a staged-wise manner, with thermal and/or catalytic reforming it provides a mixture of  $\text{H}_2 + \text{CO}$  (syngas) that can be subsequently used for the catalytic synthesis of alcohols or hydrocarbons. Further water-gas shift leads to the production of  $\text{H}_2$  upon removal of  $\text{CO}_2$ .

The technology can be applied to organic residues from diversified sources, such as sorted municipal solid waste (RDF), urban wood, agricultural residues, forest thinnings, sludges, as well as wastes from various industries, such as sawdust and pulp mill residues, spent oils, plastic-rich residues and rubber-containing wastes. The technology can also be applied to petroleum residues. It involves three main stages:

- adequate preparation of the raw material (size reduction and moisture adjustment, densification is optional);



- staged gasification initiated in a bubbling fluidized bed reactor, and pursued at increased severities in the freeboard and/or a secondary reforming unit;
- scrubbing or dry hot gas conditioning or a combination depending upon the end use.

### 2.3 How it works

Enerkem's gasification technology used low severity conditions to produce a crude syngas, followed by conditioning or cleaning of the crude syngas by subjecting the crude syngas to steam reforming, particulate removal, quenching, scrubbing, filtration and absorption prior to employing the syngas in the catalytic synthesis of alcohols (Figure 1).

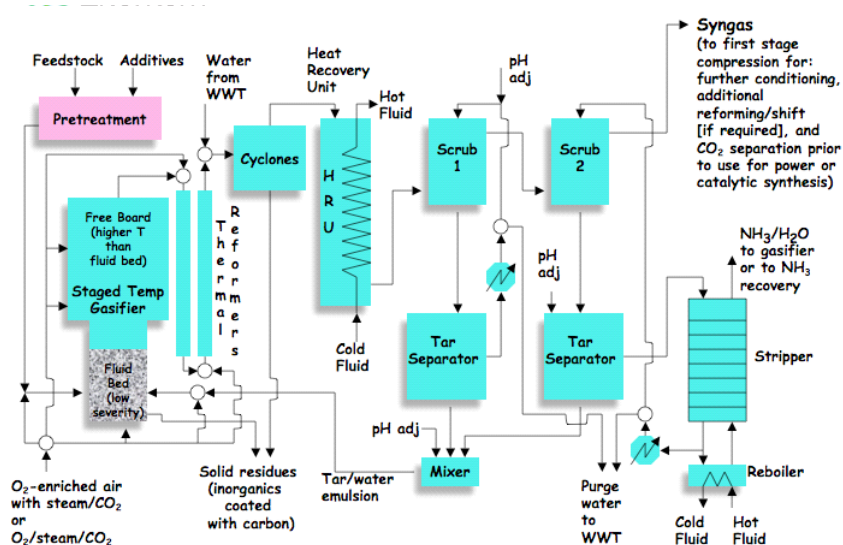


Figure 1: Syngas production from non-homogeneous biomass residues and wastes.

The waste material has to be pretreated in order to obtain a feedstock with a characteristic particle size of about 5 cm as typical dimension. The process feedstock may need to be dried (using residual process heat) since its humidity at the reactor entrance should not exceed a specific level which is a function of the feedstock composition. The bulk density of the process feedstock needs to be typically higher than 0.15 kg/l for adequate feeding to the reactor.

The feedstock prepared as described above is directed towards the gasification reactor via an appropriately designed feeding system that controls the rate of material fed to a water-cooled transfer screw that injects the material

into the fluid bed section where an appropriate fluidizing media is maintained. Injection of the needed amounts of air or O<sub>2</sub>-enriched air through a distributor grid located at the bottom of the fluid bed induces the fluidization patterns which result in high mixing and heat transfer rates which facilitate the reactions taking place during gasification. The quantity of air, O<sub>2</sub>-enriched air, O<sub>2</sub>-steam or O<sub>2</sub>-steam-CO<sub>2</sub> required, depends on the organic composition of the residues. It is usually around 25% of the stoichiometric amount required for combustion of the organics. The temperature in the fluid bed part of the reactor is kept at about 700°C. The feedstock thermally decomposes producing volatiles (permanent gases, intermediates ranging from monomers to oligomers), and aerosols (entrained tar and small particles). The thermal decomposition also produces “pyrolytic carbon” (i.e. “char”) that stays in the fluid bed until such time that its carbon content is decreased by the partial oxidation taken place in the bed and the particle terminal velocity reaches the level at which entrainment takes place towards the free board.

As the of carrier gas goes through the disengagement zone, in the ENERKEM<sup>TM</sup> process the temperature is increased by staged addition of controlled amounts of oxidant. Such addition continues in the freeboard or in a separate vessel. This exposes the volatiles and the entrained particles of char to thermal cracking and steam-driven, as well as CO<sub>2</sub>-driven reactions. Thermally induced water-gas-shift also occurs during the raise in temperature.

The composition of the synthetic gas obtained can be tailored according to the gasification agent (air or O<sub>2</sub>-enriched air), the feedstock composition, the temperature and pressure, the steam partial pressure, the fluid-dynamics and residence time distributions in the different zones of the reactor as showed in Table 1.

After separation of the larger solid particulates using cyclones, gas conditioning to achieve a clean syngas is carried out via a two-stage scrubbing process, recovering the tar and re-injecting it into the gasifier for additional syngas production. The clean syngas will contain low molecular weight hydrocarbons whose concentration depends on the nature of the feedstock.

The synthetic gas can be used for the production of energy as follows:

- combusted as is, or in combination with natural gas, using commercial boilers to produce process heat (steam);
- as a fuel, alone or with natural gas, in internal combustion engines (ICE) to produce electrical energy. Heat from the ICE hot exhaust gases can be recovered and used for steam (or other fluid) which leads to combined cycle or co-generation applications;
- as a fuel, alone (if the calorific value is sufficiently high, as when O<sub>2</sub>-enriched air or O<sub>2</sub>-steam is used rather than normal air) or with natural gas, in gas turbines to produce electrical energy via combined cycles or in co-generation mode.
- as a feedstock (when O<sub>2</sub>-steam or O<sub>2</sub>-steam-CO<sub>2</sub> are used) for the synthesis of alcohols or hydrocarbons. For this purpose the low molecular weight hydrocarbons need to be reformed.

Table 1: Biomass and Syngas composition, in low severity gasification.

Typical Biomass composition		wt%
Volatile matter		>70
Ash		1.5
Moisture		20
Ultimate Analysis		wt%
C		54.2
H		6
O		38.9
N		0.3
S		0.1
Gasification conditions		
O <sub>2</sub> /Steam/CO <sub>2</sub> gasification, low severity+ thermal cracking and reforming at higher severity		
Syngas composition		mol%
N <sub>2</sub>		2 - 6
Ar/O <sub>2</sub>		<1
H <sub>2</sub>		23 - 27
CO		21 - 23
CO <sub>2</sub>		38 - 44
CH <sub>4</sub>		6 - 8
C <sub>2</sub> H <sub>4</sub>		Traces
C <sub>2</sub> - C <sub>5</sub>		0.2 - 0.5
C <sub>5</sub> - C <sub>10</sub>		Traces
Input C converted into syngas		>90%

### 3 Syngas conversion into biofuel

Conversion of syngas to liquid fuels as well as conversion rates are directly related to the composition of the catalyst. Syngas can be efficiently converted to different products as alcohols, DME and hydrocarbons (Figure 2). Although several routes are available, a promising route at the industrial level is the production of methanol since it is a selective conversion with established catalysts and proceeds at productivity levels higher than 1 kg methanol per kg of catalyst per hour.



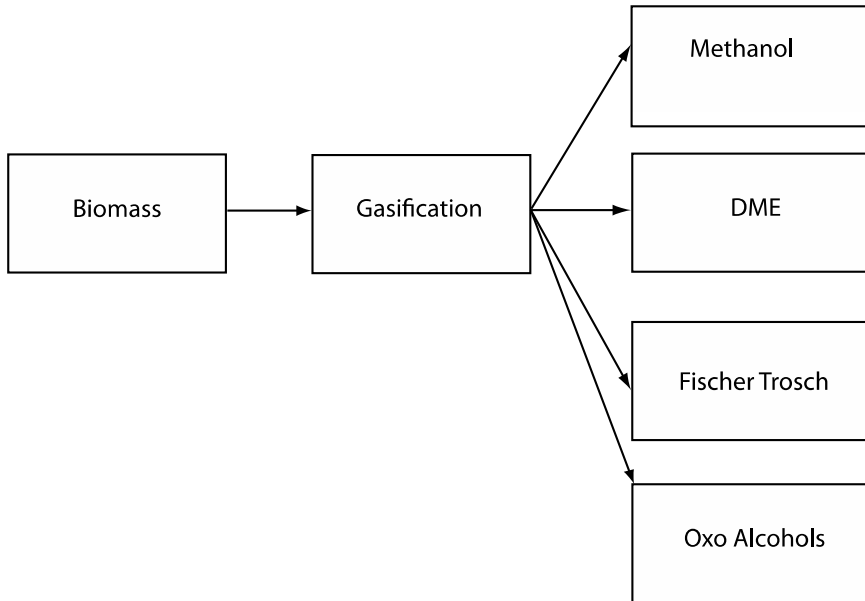


Figure 2: Examples of applications for syngas produced from biomass.

### 3.1 Syngas to methanol

The conversion of synthesis gas to methanol is thermodynamically constrained hence the need to recycle the unconverted gas to achieve high CO conversion levels. This translates into high reactor volume and increased compression costs. Methanol synthesis was carried out with the conditioned syngas using three phases reactor (slurry bubble column) in which a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst was suspended. Before the synthesis of methanol, the catalyst is reduced in hydrogen. The reductive and active form of the catalyst is CuO/ZnO/Al<sub>2</sub>O<sub>3</sub>. The principal stoichiometric reactions involved in this chemical conversion are:



It is subjected to a thermodynamic equilibrium that limits the process to low conversion per pass (CO conversion about 45%) and therefore, implies a large recycle of unconverted gas. The reaction is strongly exothermic and consequently, requires significant cooling duty.

## 4 Methanol to ethanol

### 4.1 Methyl acetate as intermediate of ethanol

Carbonylation of methanol to acetic acid or methyl acetate is a well known industrial process. It is currently performed, industrially, in a homogeneous



reaction system where a catalyst is dissolved or suspended. The Monsanto/Celanese/Eastman and BP Chemicals Cativa™ processes in the presence of rhodium and iridium respectively are conducted at moderate temperature and pressure in the presence of halide (iodide) promoters [1]. The mechanism of the reaction of acetic acid synthesis is well described in the literature and it is known as Monsanto cycle [2]. The formation of methyl acetate can be explained by the reaction between the acyl iodide formed during the reaction and the excess of methanol present in the feed.

Heterogeneous systems for methanol carbonylation have been suggested by investigators for several years. Research has been primarily focused on two possible catalysts for this reaction: rhodium supported on polymers (Acetica process is based on this principle) or zeolites and a variety of metals supported on activated carbon [3]. The choice of support seems to play an important role in the activity of the catalyst [4, 5].

In the “Energem process” [6] carbonylation of methanol is carried out maintaining methyl alcohol in vapour phase using a fixed bed packed with a rhodium-based catalyst. The methanol is vaporized under pressure and mixed with the CO-rich fraction prior to flowing through the reactor. The methanol to CO molar ratio is comprised between 1 and 4, whereas methyl iodide (co-catalyst) added to methanol is maintained at a molar ratio between 1 and 5 wt% relative to the methanol. The operating conditions are such that the GHSV (based on CO) varies between 100 to 2,000 h<sup>-1</sup>. At temperatures comprised between 170 to 300 °C and total pressures from 10 to 50 atm. It was reported that the CO is converted at rate near 100% when the methanol/CO ratio is >2. The selectivity varies as a function of temperature and pressure. It was found that within a wide range (200-240°C, 15-50 atm) for the specified GHSV (Based on CO) range, molar selectivity of 50-75% methyl acetate and 25-50% of acetic acid.

#### 4.2 Methyl acetate hydrogenolysis: synthesis of ethanol

Methyl acetate produced as previously via carbonylation, is maintained in liquid form at 20°C. It is pumped in a pressure vessel ranging from 10 to 50 atm, through a heat exchanger that vaporizes it at temperatures ranging from 150 to 225 °C. Preheated hydrogen in the same temperature range is mixed with the methyl acetate vapour at the exit of the heat exchanger. The molar ratio H<sub>2</sub> to methyl acetate is from 5 to 11. The hot mixture is flown through a catalytic bed where a CuO/Cr<sub>2</sub>O<sub>3</sub> or CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst is placed. The CuO is reduced with H<sub>2</sub>/N<sub>2</sub> mixtures prior to adding any methyl acetate [7]. Methyl acetate is converted to methanol and to ethanol at GHSV (based on H<sub>2</sub>) comprised between 1,000 and 2,000 h<sup>-1</sup> and the methyl acetate conversion is up to 95%, with a higher selectivity in ethanol.

### 5 Conclusion

Energem has successfully proven, at pilot scale, the feasibility of converting heterogeneous biomass residues into a homogeneous syngas that can be used for



the synthesis of methanol. The latter is a key intermediate building block for chemical commodities and biofuels such as bio-methanol and from the latter bio-ethanol. The technology is applicable to any organic material and residual biomass including urban biomass such as residential waste. It is preferable that the waste sorted to remove recyclables as well as ferrous metals, glass and ceramics. Typically, to maintain consistent performance, inorganic matter levels should be kept below 20 wt% in the feedstock (dry basis).

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