The Equivalence Ratio: The Key To Understanding Pyrolysis, Combustion And Gasification of Fuels

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In 1979 Tom Reed and Ray Desrosiers calculated the equilibrium temperatures and compositions for biomass thermal conversion to heat or gas. We produced the diagram below (simplified here) as part of a comprehensive study of Biomass Energy. (Originally published as SERI/TR-33-239; now reissued from the BEF Press as "the Encyclopedia of Biomass Thermal Conversion).

Through the years I have found that at temperatures above ~700 C, the equilibrium calculations are close to those measured, so this is my roadmap to biomass pyrolysis, gasification and combustion. I have continued to use and add to the detailed calculations in this study and I hope that the following will be as helpful to others as it has been to me.

THE EQUIVALENCE RATIO, Φ: For any process,

Φ = the actual air fuel ratio/the air fuel ratio for complete combustion

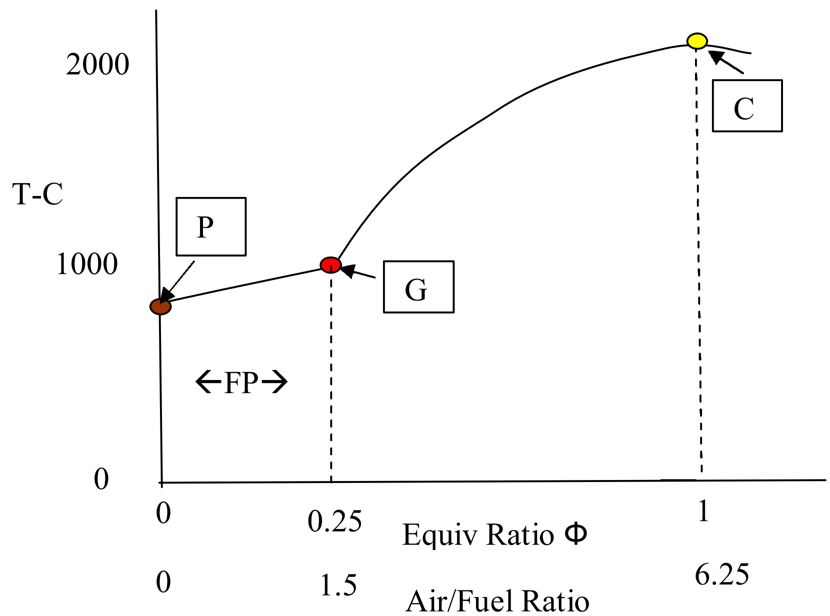
The ER diagram is given below for biomass, but looks quite similar for all other fuels. The points P, G and C show the ideal ER for pyrolysis, gasification and combustin. The area FP is a zone between pure pyrolysis (P) and isothermal gasification (G) in which smaller amounts of air produce mixed pyrolysis and gasification.

A necessary compliment to the ER for exact calculations is the Air/Fuel (A/F) ratio. Hydrocarbons and biomass have very different compositions, so for final calculations it is also necessary to calculate the actual air/fuel ratios from the fuel composition.

Biomass is a mixture of ~50% cellulose, 25% hemicellulose and 25% lignin, so has no "exact formula". Neither does "oil" or "coal", so for detailed calculations you will need an ultimate analysis. However, generic formulas are sufficient for many calculations. Here are my "generic formulas, sufficient for many calculations:

Natural gas	CH_4
Hydrocarbons	CH_2
Coal (and aromatic HCs)	CH
Biomass	$CH_{1.4}O_{0.6}$
Carbohydrates (sugar, cellulose, …)	CH_2O

We find that on a dry ash free basis most "biomass" falls in a narrow range of composition. In our calculations the "carbon ratio formula" for typical biomass (dry, ash free basis) was taken to be $CH_{1.4}O_{0.6}$. The high heating value for this composition is 22.2 kJ/g (9550 Btu/lb) and the low heating value is 21.0 kJ/g (8987 Btu/lb). Using these values we calculated the equilibrium temperature for the reaction of biomass as a function of equivalence ratio and the results are shown in the Figure below. (We also calculated values for various other values of pressure, moisture and oxygen, see original calculations.)



THE EQUIVALENCE RATIO AND AIR FUEL DIAGRAM

(Air/Fuel values shown for biomass)

COMBUSTION (Point C in figure): Combustion reaches a maximum temperature when the air fuel ratio permits all of the hydrogen and carbon in the fuel is burned to H_2O and CO_2 (stoichiometric combustion). Since combustion is the ultimate destination of most conversion processes, it is the most important benchmark of gasification, pyrolysis and flaming pyrolysis.

The formula for stoichiometric combustion with oxygen is:

$$CH_{1.4}O_{0.6} + 1.05\ O_2 \rightarrow CO_2 + 0.7\ H_2$$

(Calculations for air combustion require adding 3.78 N2 for each O2 on each side of the equation.)

For dry, ash free air combustion, this produces an adiabatic flame temperature of 2025 ºC, similar to most other combustion temperatures. (Of course there is no DAF biomass and you must trim this number to take account of moisture and ash.)

CONVENTIONAL GASIFICATION (Point G in figure): Optimum conventional gasification occurs at ~ 0.25 equivalence ratio air (or oxygen) at a temperature of °C and produces a gas whose active ingredients are CO and H_2 with as little free carbon as possible. (See point G in figure below.) The break in the curve at

0.25 is due to the disappearance of carbon at higher values, since carbon production is exothermic.

PYROLYTIC GASIFICATION (PG) (Point P in figure): Pyrolytic Gasification (PG) operates at 450-600ºC with an external heat source to produce a rich flammable gas plus free carbon (~20-30% and mineral ash). The flammable gas can then be burned or converted to synthesis gas in a second process by steam or oxygen reforming. The carbon/ash can be used to power the process or for carbon credits and fertilizer. Unfortunately ~30% of the product is a low temperature tar which can also be converted to a cleaner gas by air, oxygen or steam gasification.

FLAMING PYROLYTIC GASIFICATION (FPG) (Area FP in figure): Flaming Pyrolytic Gasification (FPG) uses smaller amounts of air/oxygen passing through a bed of biomass to generate gas plus carbon/ash at ~700ºC. We have built a number of transparent research gasifiers in which the effect is very evident.

The flammable gas can then be burned or converted to synthesis gas in a second process by steam or oxygen reforming. The carbon can be burned in the same or a separate process to give additional heat if needed for converting the tars to more gas or used for carbon credits and fertilizer. The BEF WoodGas stove uses FPG to generate gas for cooking and incidentally generates 5-25% charcoal, depending on moisture content of fuel.