Gasification and Pyrolysis of Coal, Biomass and Wastes

Basic Principles and Applications

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By

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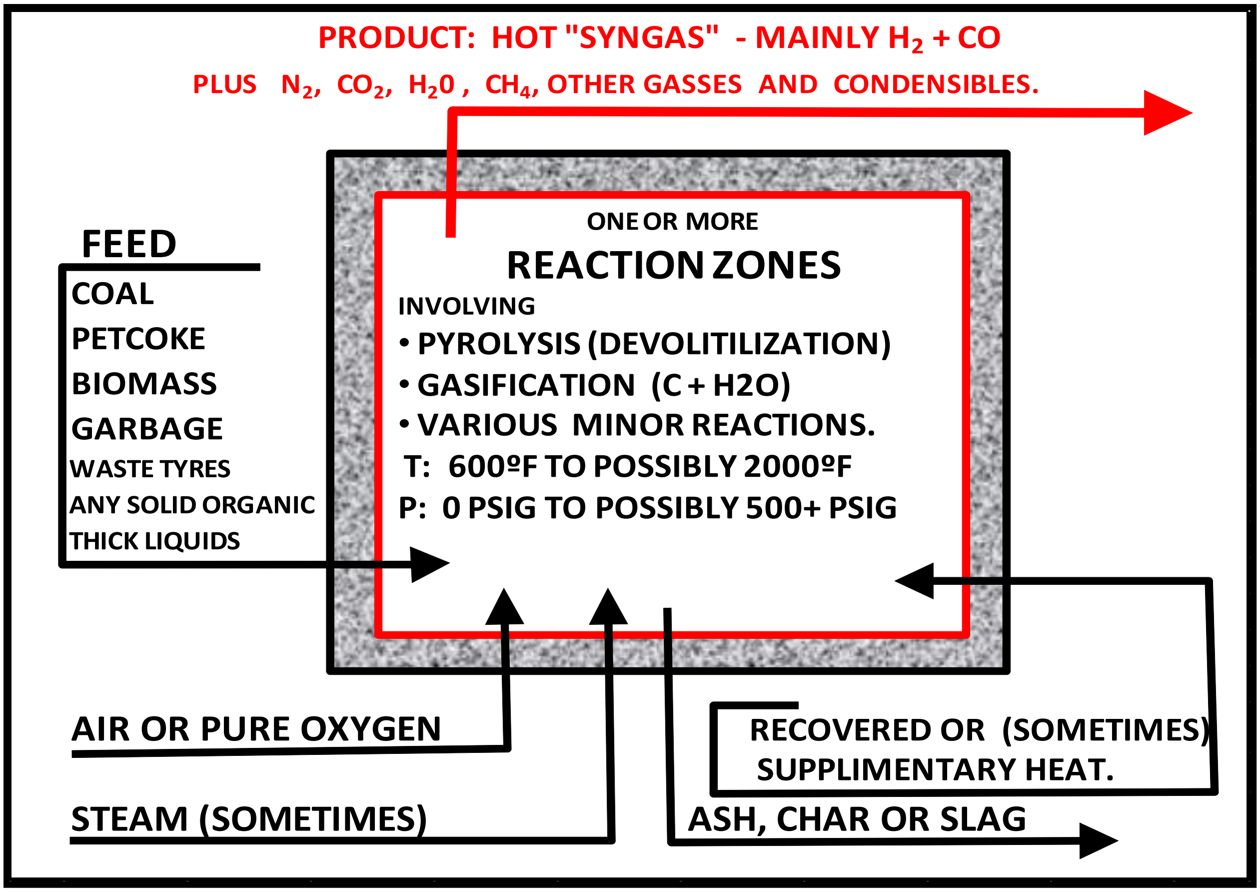
1. Introduction

Scope

This course is designed to provide the basic knowledge, of chemistry and physical properties, to design equipment for gasification and pyrolysis processes, and to analyze and understand existing or proposed designs for such equipment. Since the current “state of the art” can be called uncertain or pending, currently operational technology will only be covered cursorily, with specific examples to demonstrate the basic principles. Economic factors will be mentioned, but with no data or estimates. This scope covers specific equipment wherein the essential gasification, pyrolysis or other essential reactions take place. Details of equipment for solid feed preparation and recovery or separation of products, covered by normal Chemical Engineering Best Practice will only be described briefly. This course will also include examples of how gasification and pyrolysis processes have failed to perform as designed or expected, due to factors frequently over-looked in their design, all involving physical properties of feed or products.

Definitions

Gasification is the combination of thermal processes to convert any combustible carbonaceous solid to a clean mixture of gases, to be used either for combustion to generate electricity, or for chemical synthesis to produce liquid fuels or other useful products. Pyrolysis is the first step in a gasification sequence, consisting of devolitization or partial vaporization of solid feed.



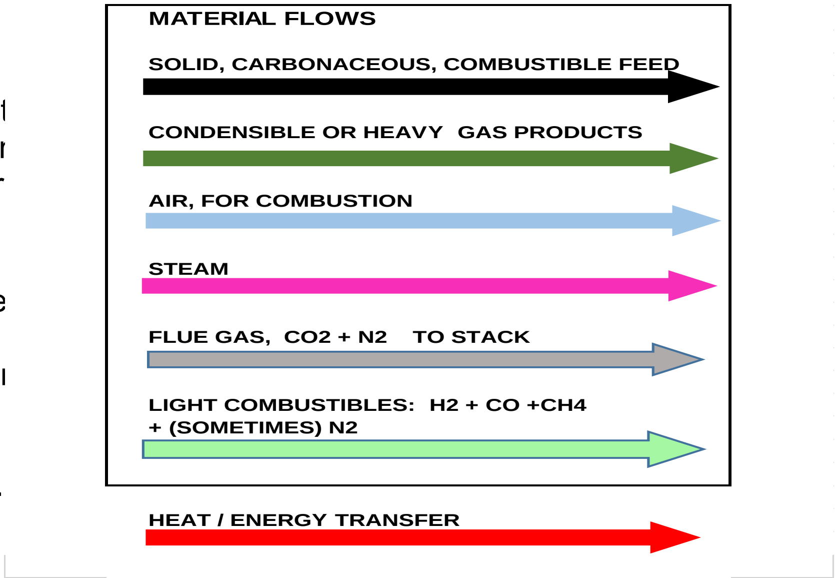
Importance

Gasification and Pyrolysis are the essential steps to all process for thermal conversion of solid carbonaceous materials to liquid or gaseous products, and for non-polluting combustion of coal, biomass or waste materials for electric power – plus a wide range of industrial processes. For future development of completely non-polluting coal applications and greatly expanded production of synthetic fuels from biomass and various wastes, understanding of these process steps will be essential.

Kinds of Processes

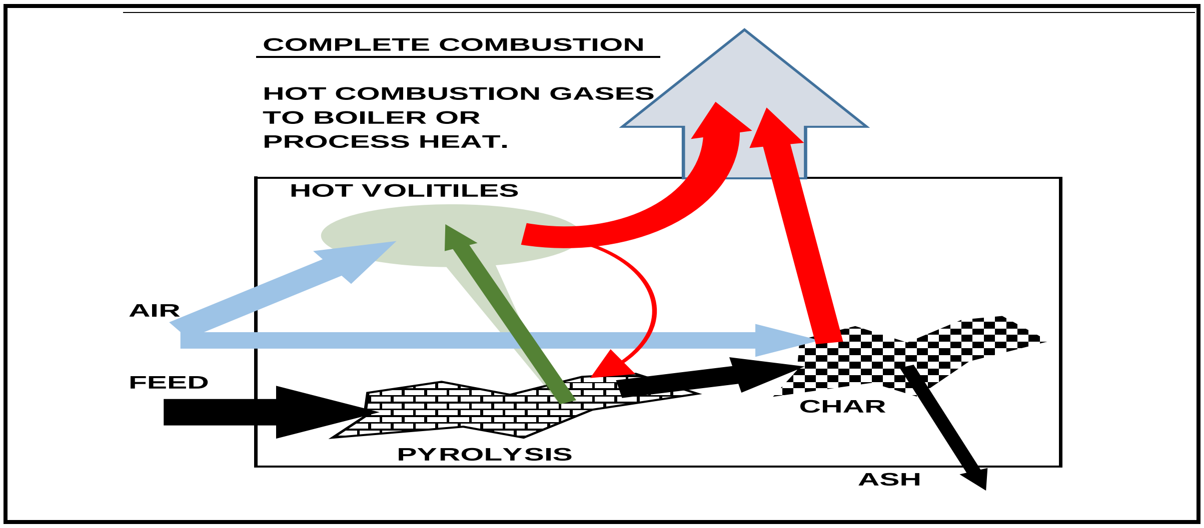
Workable processes covered by the above general definition, can be classified into four categories, as defined by the illustrations below, in t simplest terms possible. Maternal ar energy transfers are color coded per this legend.

Any/all of these may be accomplishe any temperature or pressure. Combustion steps may use air or pu oxygen. The rates and yields of the steam gasification group may be modified by the addition of catalysts.



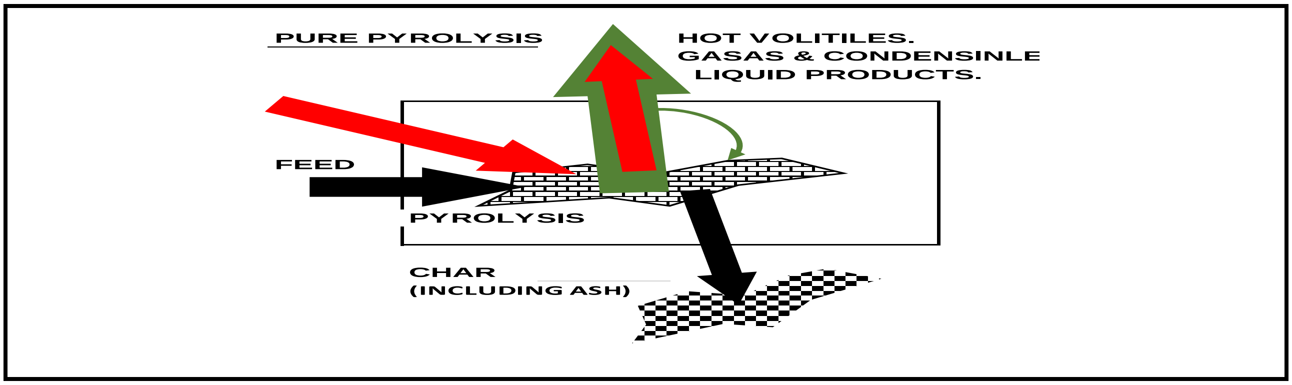
The following diagrams define the mass transfers involved in the important reactions involved in the various gasification and pyrolysis process steps. All of them assume dry feed. As feed particles are heated to reaction temperatures, the first thing that happens is simply drying, or vaporization of all moisture from the particles, which is usually completed before the particles each about 120ºC.

(1) <u>Complete Combustion</u> of any solid feed (coal, biomass, wastes)
Traditional, simplest process to extract heat from any solid immediate proximate use. This describes the function of oldest power generation systems. Efficiency is maximized by direct combustion of volatiles and char, with little or no heat loss before utilization at boiler tubes, or process heat. In some cases higher quality (HHV) gas, at higher temperature, can be produces by expensive use of pure oxygen.



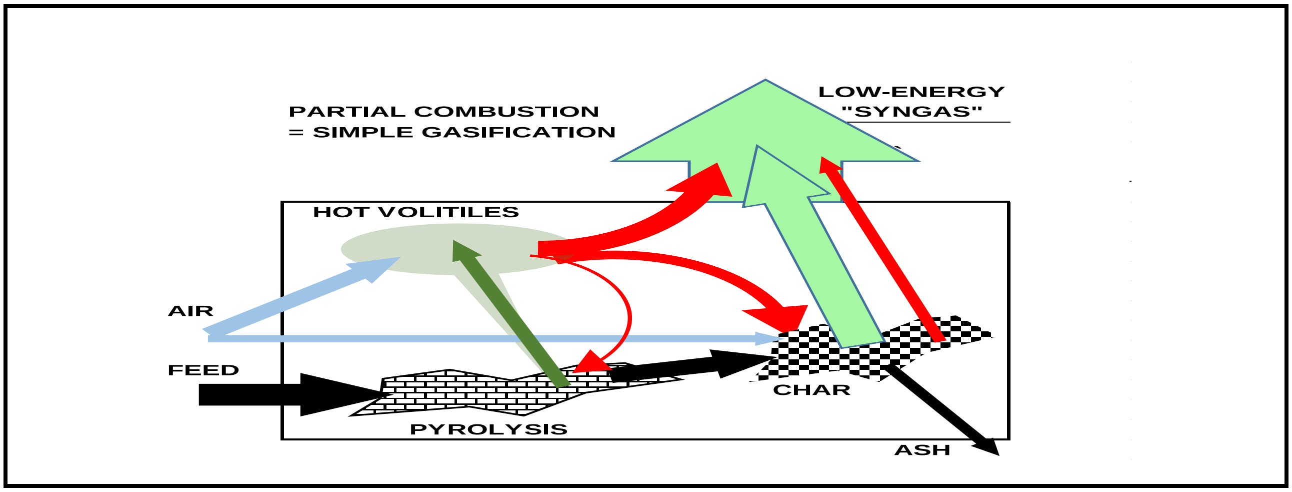
(2) <u>Pure Pyrolysis</u> of solids by external heat source.

Use of external heat, with no combustion of feed, to liberate volatile materials, both condensable liquids and non-condensable gases, from any solid, always leaving a non-volatile carbonaceous char or other residue. Product gases and condensables are of high quality (HHV or desired chemical content) due to lack of dilution by products of combustion. None of the feed is consumed to provide heat. Effective heat transfer is the primary, limiting design factor.



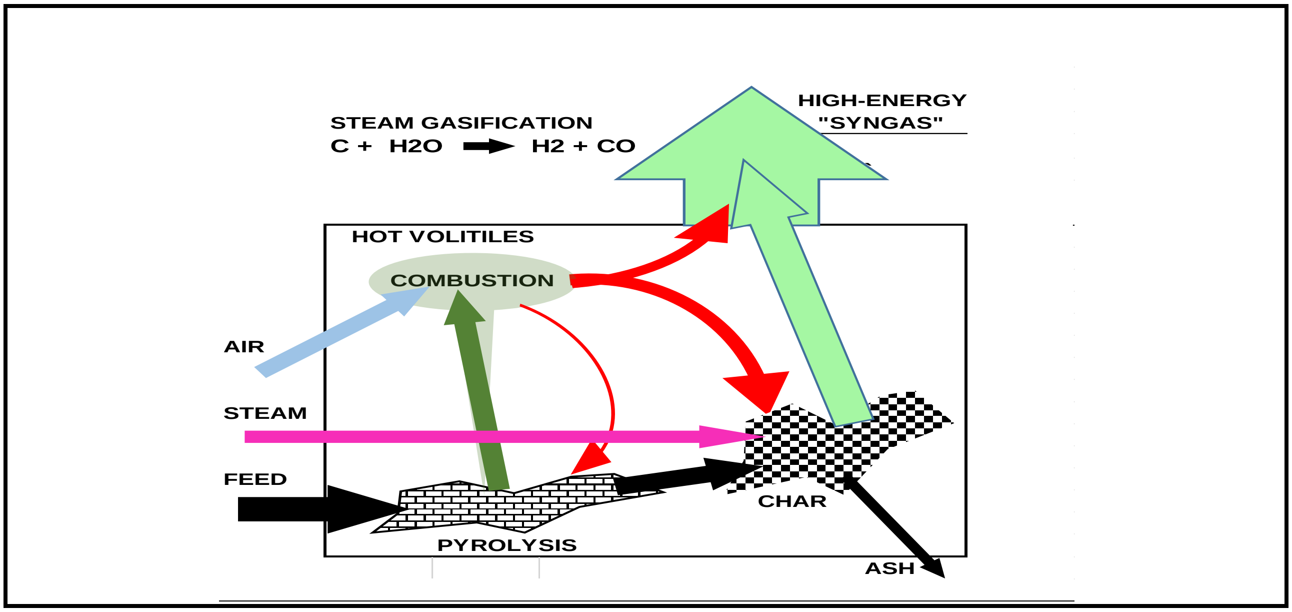
(3) <u>Partial Combustion</u> or Simple Gasification for directly used fuel gas.

Gas may be burned/consumed remote from origin or used for synthesis of other products. Pure oxygen may be used instead of air, for higher quality (energy content) gas. Maximum release of feed HHV is delayed until final combustion of H_2 & CO at point of use. Various gas cleaning steps may be added between partial and final/complete combustion.



(4) Steam Gasification for High Energy “Syngas.”

This area covers most of the current, large scale, “state of the art” processes for production of high value gas (maximum H_2 and CO, with minimum CO_2) for fuel or further adjustment for syntheses of other products, at a cost of lower overall efficiency due to energy consumed by the endothermic steam-char reaction.



2. Chemistry

Essential Reactions

The dominant reactions in involved in all gasification processes are as follows. (Numbering corresponds to above process definitions.) Reactions in red are endothermic, consuming energy. Those shown in black are exothermic releasing heat.

(2) Pyrolysis

$C_XH_YO_ZS_W \longrightarrow C, CO, H_2, H_2O, CH_4, C_2+, H_2S$, Tar, Oil, & PICs

This reaction rate is wildly variable, depending on the composition of feed and the rate of heating individual particles. The reactant may the solid feed or various heavy HCs as volatiles. Intentional pyrolysis normally occurs in the reaction zone, close to the surfaces of solid feed particles, as heavy PCs are vaporized. But ----- See reaction (9).

	Approx. DH Kcal/kmol	**"CGE"**
(1) Complete Combustion		
$C + O_2 \rightarrow CO_2$	-1,000,000	N/A
(3) Partial Combustion		
$C + 1/2\ O_2 \rightarrow CO$	-36,000	65.3%
(4) Steam-Char Reaction		
$C + H_2O \leftrightarrow CO + H2$	+32,000	131%

DH = Heat of Reaction: + = Endothermic - = Exothermic
PIC = Products of Incomplete Combustion
CGE = Cold Gas Efficiency = (Calorific value of products) / (Calorific value of reactants.), ignoring any sensible heats or enthalpies. Therefore:

- The steam-char reaction is the primary source of the desired projects and should be maximized.
- In any gasification process, partial combustion is the primary and preferred source of process heat.
- Some complete gasification is inevitable, but should be avoided as possible, as it consumes carbon, detracting from CO production.
- The majority energy liability, detracting from overall thermal efficiency (besides the mechanical energy costs, like air compression & external steam generation) is the steam-char reaction

LESSER CONCURRENT REACTIONs.   (All exothermic)

(5) Water-Gas-Shift

$CO + H_2O \leftrightarrow H_2 + CO_2$ + Heat

This reaction may occur, in either direction, during gasification, but is an essential step, achieved in subsequent reaction vessels, to adjust the H_2/CO ratio as needed for downstream synthesis steps.

(6) Char Methanation or Hydro-gasification.

$2H_2 + C \leftrightarrow CH_4$ + Heat

(7) Methane Synthesis

$3H_2 + CO \leftrightarrow CH_4 + CO_2$ + Heat

(8) Boudard Reaction (Soot formation)

$2CO \leftrightarrow CO_2 + C$

These reactions may or may not happen to a significant extent in the reaction zone – depending on many conditions but may be important to downstream process objective. They are all reactions that may be intended in the particular process design and hopefully controlled and optimized, as discussed later. Note that all are equilibrium dominated, and will proceed in either direction, quite rapidly, as determined by temperature, pressure and concentration of products and reactants.

Priority of reactions: At any point where free O_2 is available, gas phase reactions will occur first, heavy condensable vapors will then pyrolyze and burn. Heavier, condensed droplets pyrolyze and burn next. Finally, available will proceed to burn residual carbon. In a well-mixed combustion atmosphere, condensable pyrolysis products should not survive.

(9) However -(to assure that Murphy's law applies)- **delayed or reverse pyrolysis** may occur anywhere in the reaction zone or beyond, resulting in gooey, sticky tar or carbon deposits, where they are neither expected nor welcome. Such reactions are cause of most of the unexpected problems that occur in initial operation of new equipment. (This area is generally glossed over by chemists and pure process engineers, and left to final designers of specific equipment to worry about.)

Chemical Properties

All feedstocks are primarily defined by the following standard tests.

PROXIMATE ANALYSIS – Components removed by increasing temperature to 950 ºc (1650ºF) in a neutral atmosphere (Argon). This is a universal, standard laboratory test, which predicts what products, as defined, may be obtained by complete pyrolysis.

Moisture (To 220ºF)
VM: Volatile Matter
FC: Fixed Carbon (Stable Char) remaining above 950ºC.
Ash (Mineral Matter, after adding air to burn away FC)

ULTIMATE (ELEMENTAL) ANALYSIS – Dry, ash-free basis: C, H, O, S, N, P, Cl

ASH (MINERAL) ANALYSIS – By X-ray diffraction: Si, Fe, Ca, K, Na, Ti and any other metallic elements present in significant amounts.

CHEMICAL EQUILIBRIUM

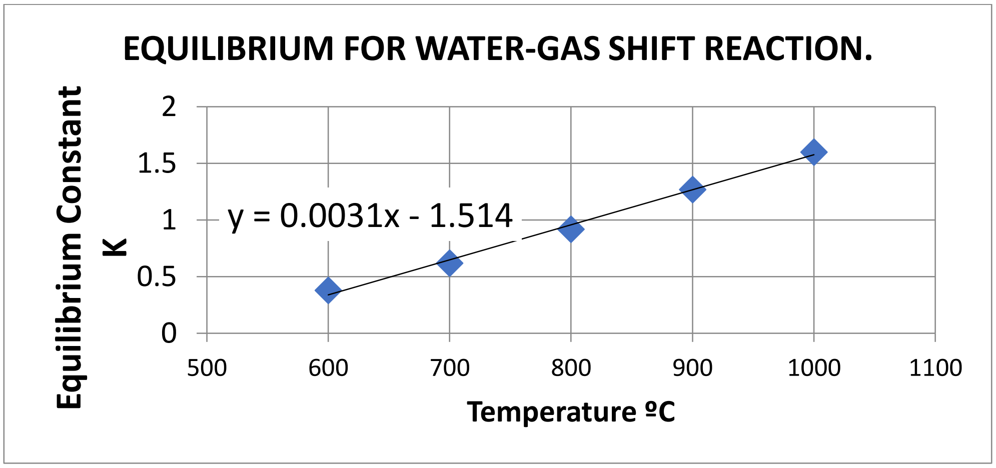
In an environment of mixed gasses, all reversible reactions (“↔“) will proceed to some degree of completion, determined by the relative concentration of reactants and products, and an empirical constant for the specific reaction.

Reactions 1, 2 & 3 go spontaneously to completion

Reactions 5, 6 and a few lesser ones are equilibrium-driven: They proceed rapidly to some degree determined by their equilibrium constant --

$K = (P_1 x P_2 x P_3 \ldots.)/(R_1 x R_2 x R_3 \ldots.)$ where P & R = partial pressures or molar concentrations of Products and Reactants.

Example: $CO + H_2O \leftrightarrow H2 + CO_2$ $K = (CO_2)x(H_2O) / (CO)x(H_2)$



So, at equilibrium the hydrogen concentration, in whatever units, should be:

$(H_2) = (CO_2)(H_2O) / K(CO)$,

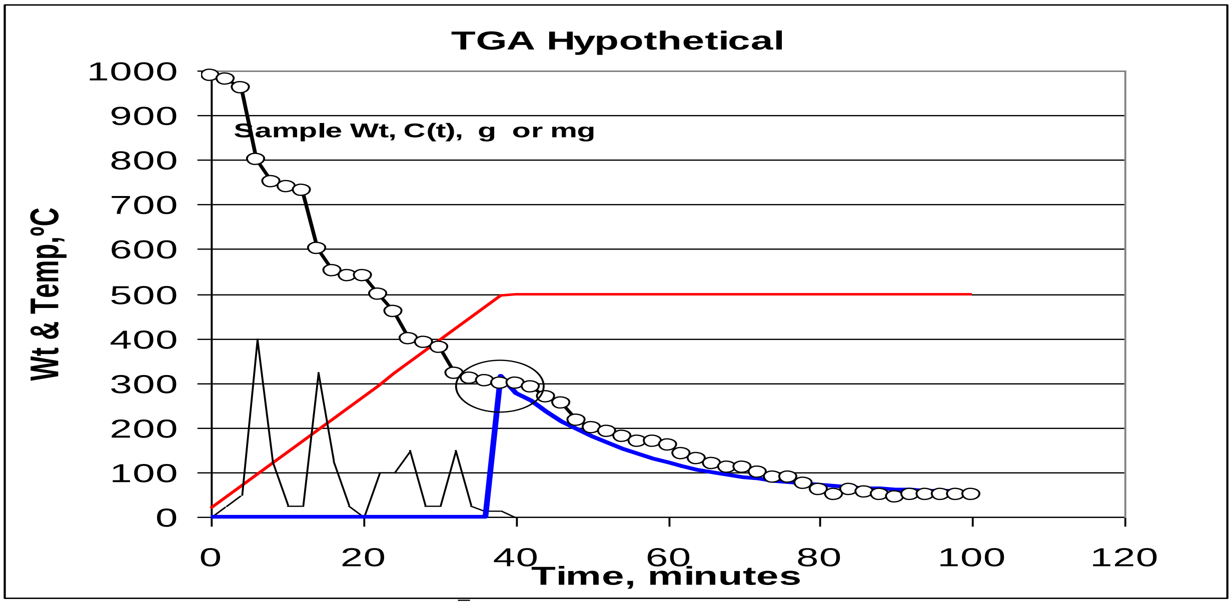
where K is a unique, experimentally determined value, for each material.

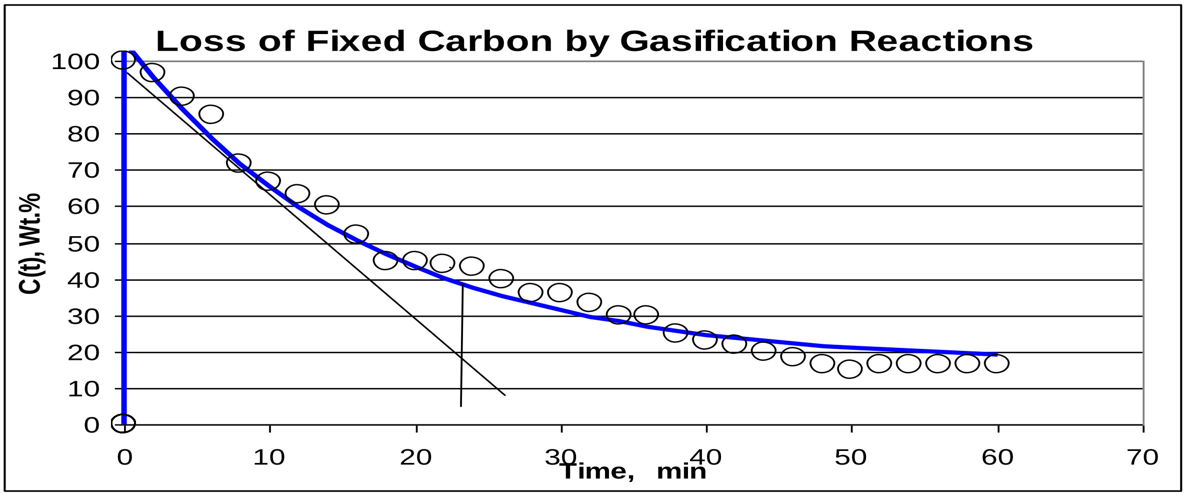
THERMO**G**RAVIMETRIC **A**NALYSIS (TGA)

This a generally accurate laboratory prediction of the reaction that can be expected from the steam-char reaction (4), following drying and pyrolysis of the feed. It is a critical characterization of the suitability of candidate feed for production of a Syngas. It predicts the rate at which the reaction approaches completion, and thus residence time, throughput capacity or size required of a gasifier vessel. In the standard procedure for this test, a small sample is placed on a scale enclosed in a small heated – and sometimes pressurized – test vessel, See example data below. With a flushing flow of Argon, the temperature (Red line) is ramped up to the desired test temperature, T_0, and then held constant, as Argon is replaced by saturated steam. The sample weight (Black and blue lines, Scale not shown.) is continuously recorded. When temperature reaches T_0, all moisture and VM (Volatile matter) will have been removed, by drying and pyrolysis, leaving only FC (Fixed Carbon), which begins to react with the steam. ($C + H_2O \leftrightarrow CO + H_2$) T_0 may be as high as 950oC, or the maximum temperature in an anticipated gasifier design.

This is a first order reaction, in which the carbon is consumed at an exponential rate, in proportion to the amount remaining. This part of the curve (Blue line) is reported separately, as shown in the second plot below.

TGA = ThermoGravimetric Analysis





C(t) = C_0 + C(t) e-kt, which h describes a “first order reaction,” where dC/dt = k C(t).

T_0 = Temperature Set Point, at which all volatiles are flashed off and only FC remains.

C_0 = Wt. of Ash, after all FC is consumed.

C(t) = Wt. of FC + Ash, starting at $C(T_0)$. Defined as 100%.

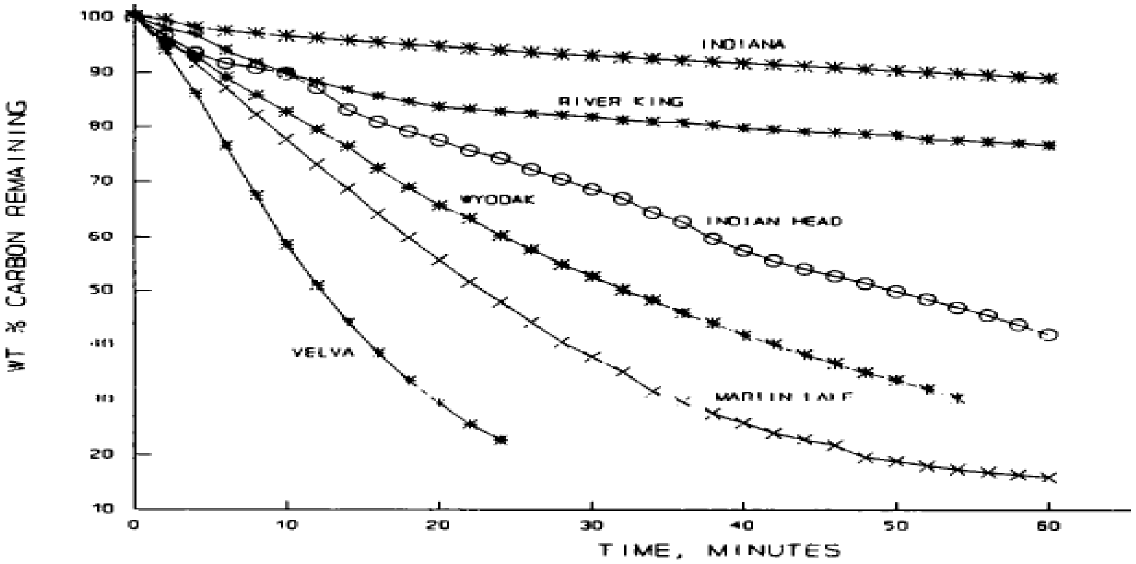
k = Initial slope of the exponential decay curve, usually reported in **reciprocal hrs, h^{-1}**.

In this example, k = 22 min = 0.37 hours = 2.7 h^{-1}. This is then the reported Reactivity of the sample tested.

As an example of the wide range of this variable, the plot below shows actual TGA data for 6 US coals. Note the wide variety with “rank” or geologic age of coal. Velva & Indianhead are Lignites (Cenozoic), Wyodak is a Subbituminous (Mesozoic). Indiana is Bituminous (Earlier Mesozoic)

Note that the lignites, though of low HHV (higher heating value) due to high ash and moisture contents, mined mainly in mid-western plains states, are far more reactive than the more valuable “high rank” eastern coals from Appalachian and Ohio Valley deposits. Biomasses can be considered “coals” of geological age zero.

Raw TGA Data for Several Coals.



CATALYSIS

Besides the geological age of coals, Reactivity is also affected by the content of alkaline metals, mainly K and Ca, in the feed. These elements, in the reducing atmosphere of a steam-char reaction zone, function as catalysts, enabling and the reaction. They are in either an active ionic, or possibly a metallic vapor phase, briefly bonding to the carbonaceous structure, participating in the reaction. (This also applies to the reaction (6), 2H2 + C ↔ CH4).

In coals, the content of catalytic elements may be quite high, but may be mainly in the form of various refractory aluminosilicate minerals, and so are not released at gasification temperatures, up to 900^{o}C, but remain locked in the ash. In wood, by contrast, these elements, mainly K, are incorporated directly in molecular structure, mainly of lignin, which completely disintegrates during pyrolysis, releasing the metals in active, catalytic form. Low rank, geologically young (50~100 MY) coals, like lignite, have a molecular structure less completely modified from, their original lignin, and thus retain K and Ca in more reactive form than say bituminous coals or anthracite (300 MY+)

Substantial research has been done, up to pilot scale, impregnating coal and wood feeds with various soluble alkaline materials, to accelerate the gasification rate, and thus greatly reduce the size of the expensive reactor vessels. This raises the question of how much added alkaline catalyst can be added and how far the reactivity can be accelerated. Catalytic impregnation, with K_2CO_3, for example, can get quite expensive, compared with simply recycling wood ash. The Table below shows some data on the relative effect of added catalysts on different coals and wood.

At present, commercially operational technology, gasification process are *probably* relying on the effects of catalytic elements inherent in the feedstocks. In addition to accelerating gasification rates (Reaction 3, above) it is also effective for hydrogasification (Reaction 6).

Examples of TGA Data for Coals & Woods Showing Effects of Catalyst Addition.

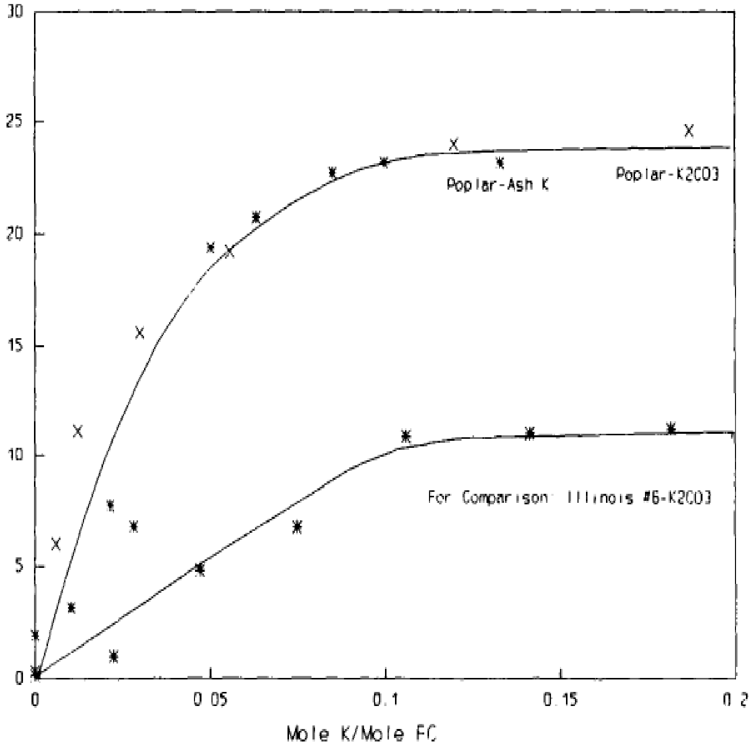
(Reactivity units: $k = hr^{-1}$)

Temperature	°C	650	700	750	800
	°F	1112	1202	1292	1382
Bituminous Coal	Raw		0.07	0.33	0.34
	20% Limestone			0.50	1.45
	10% K_2CO_3			4.36	
	10% K_2CO_3 + Limestone			5.38	
	19% Hot Ash Leachate		0.61	3.01	5.15
Subbituminous Coal	Raw	0.37	1.31	1.76	3.05
	10% K_2CO_3	1.25	4.30	8.28	12.48
Lignite	Raw	0.30	1.35	2.10	1.56
	20% Limestone	0.48	0.81	6.49	15.50
	10% K_2CO_3	1.25	4.06	8.17	34.90
Wood (Species not reported)	Raw		0.13	0.33	1.10
	10% Wood Ash		4.18	5.84	18.24

In addition to increasing rapidly with temperature, these reaction rates also increase with the amount of catalyst added, reported as catalyst/FC, mol./mol. The effectiveness of the catalyst depends on the intimacy of getting the catalytic element (K, Na or Ca) bonded to the active sites on the carbonaceous particle surfaces. Impregnating the feed with chemically mobile K^+ ions, by soluble K_2CO_3, is thus more effective – and expensive – than simply blending recycled ash with the feed.

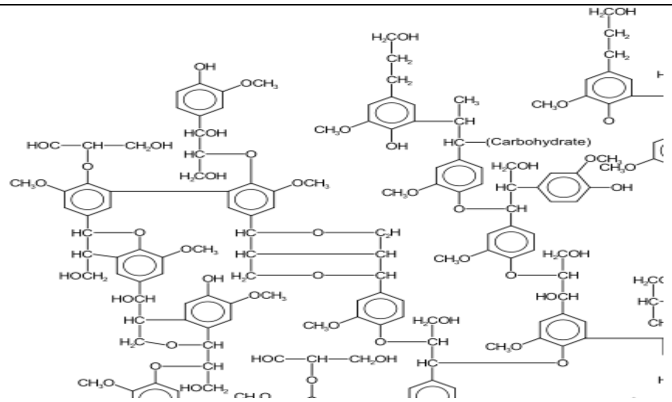
('Apologies for the limited legibility of the following graphic, and a few more later. Quite unavoidable.)

Here are some laboratory data plots showing the relative increase in reaction rates with increasing amounts of K2CO3 impregnated on the raw feed.   The lower curve is for slow-reacting bituminous coal (“Illinois No. 6”) and the upper curve is for fast-growing hybrid poplar wood (Plains Cottonwood x European Black Poplar). The difference is due to the relative density of active sites on the molecular structure of the carbonaceous surfaces. The saturation levels indicate the limited availability of such sites. The extended structures are not completely uniform. Some probable models are shown below.



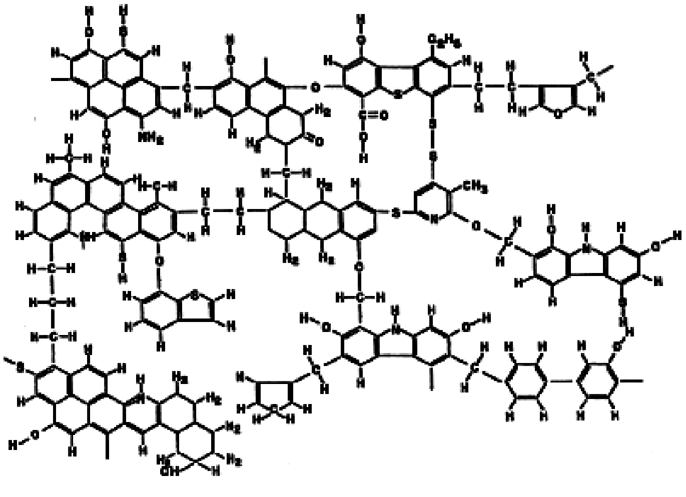
LIGNIN

Approximate molecular structure of lignin, the primary component of woody biomass tissue. Structure is semi-random, non-repeating. Note profusion of $-OCH_2$ and $-CH_2OH$ sites which may be ionizable with H^+ replaced by Na^+, Ca^{++} or K^+ ions. Through geological time this structure condenses to more random, all-rings structure of coal, as shown below.

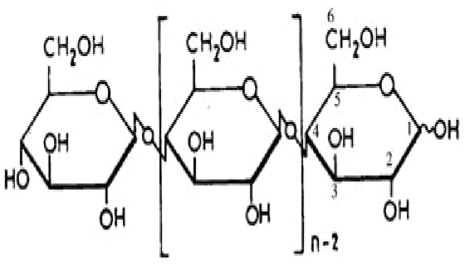


Once dead, the cellulose in plant materials tends to decompose rapidly, while the more durable lignin, once entombed in a compressed, completely anaerobic environment, very slowly – over millions of years, as the durable carbon rings condense into the more dense structures typical of coals.

COALS
Typical/proposed chemical structure of coals. Compared with lignin, above, note loss of most or all of -OCH_2 and -CH_2OH sites, where catalytic metal atoms could attach. This loss is more complete in older coals, accounting for their lower reactivity. Unlike biomasses, coals may have much or their alkali metals, that show up in an elemental analysis, combined in mineral grains as refractory aluminosilicates, and thus not available for catalysis.

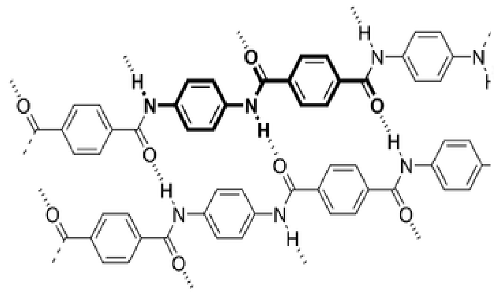
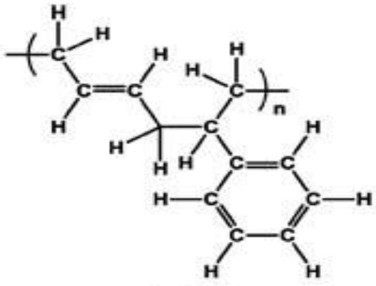
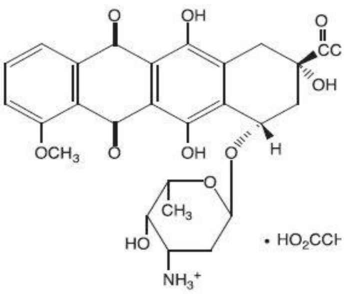


CELLULOSE.
Complete biomasses, such as crop waste, that are high in leaf and non-woody stem tissue, may be composed of more cellulose than lignin. (Cellulose is by far Earth's most common organic compound.) It is a very orderly, much simpler structure, with the carbon rings connected as long chains. Wood consists of cellulose fibers, bound together by dense lignin binder. These fibers, separated from the lignin, are the major component of paper and cardboard, which in turn are major components of municipal/domestic solid waste.



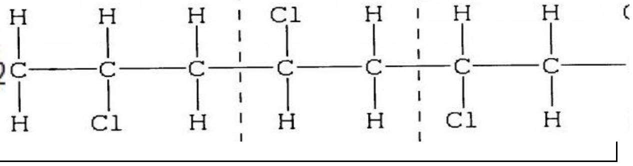
During pyrolysis, the non-cyclic appendages of these structures are the first parts to break off as the more refractory carbon rings tend to condense ever more tightly. Some of the rings are also devolatilized as heavy, tarry condensable vapor components. Man-made materials, like plastics and synthetic rubber, in contrast to lignin and coals are made of very order, long chain molecules, cross-linked in also-orderly ways.

RUBBER
There are many formulations for synthetic rubbers, mostly for tires and other very durable products, and some for more fragile, flexible products, such as condoms and surgical gloves, where they compete with natural rubber.

PLASTICS

Most plastics, occurring in large volumes in municipal garbage, are extended polymers of simple, no-rings monomers that are rapidly pyrolyzed. Some, like polyethylene, in final stages of pyrolysis can condense into residue of more coal-like structures that can be eventually burned or gasified.

Polyethylene	Polyvinyl chloride (PVC)
$-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2$	

SUMMARY OF DESIGN OBJECTIVES IN BALANCING UTILIZATION OF THE DIFFERENT CHEMICAL REACTIONS INVOLVED IN GASIFICATION OR PYROLYSES PROCESSES.

Where syngas is to be burned for heat or electricity –

- Maximize overall thermal efficiency, from fuel to flame.
- Avoid pollutant carry-over (SOx, NOx, Particulates)

Where syngas is desired for some downstream synthesis –

- Deliver a required proportion of H_2/CO
- Maximize the total yield of H_2 + CO
- Maximize overall thermal efficiency, from fuel to syngas.
- Avoid pollutant carry-over (SOx, Nox, Particulates)

Where gas and condensable pyrolysis products are desired –

- Achieve complete devolitization, leaving pure carbon product.
- Achieve optimum desired distribution of volatile products.
- Maximize overall thermal efficiency, from feed-plus-heat to products.

Considering the basic reactions, do you notice the contradiction in these objectives? So, trade-offs must be devised.

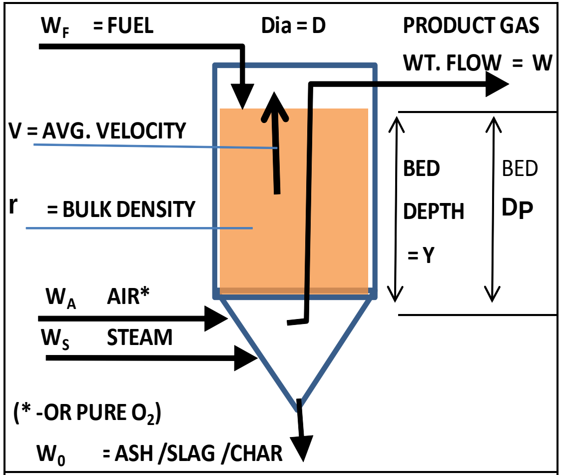
3. Physical Design Criteria

At this point, you are now an expert on the chemistry of gasification and pyrolysis, and no doubt ready and eager to look at actual process. But before that, you must understand the physical properties of feed materials and how they change during the reactions covered above. It is these properties that determine whether a process will function as designed or function at all. Following this Section, Applications will be presented, with actual case studies, describing things that went wrong and why. So please have patience.

HOW TO DESIGN A GASIFIER

First of all – gasifier design is pretty much empirical. It starts with trial and error lab work to guesstimate process conditions to implement the desired chemistry. It requires only a few basic calculations as used in the design of any packed or fluidized bed. **For the majority of possible gasifiers**, these are as follows. Some alternative, less common, gasifier designs and pyrolysis vessel design will be introduced later, with specific applications.

"FIXED (PACKED/SETTLING/COLLAPSING) BED"



BED ROUGHLY DEVIDED INTO ZONES, FROM BOTTOM UP: COMBUSTION, GASIFICATION, DEVOLITIXATION, DRYING.

$W = W_A + W_S + W_F - W_0$, Lb/hr

DP x Area must be < Wt of bed.

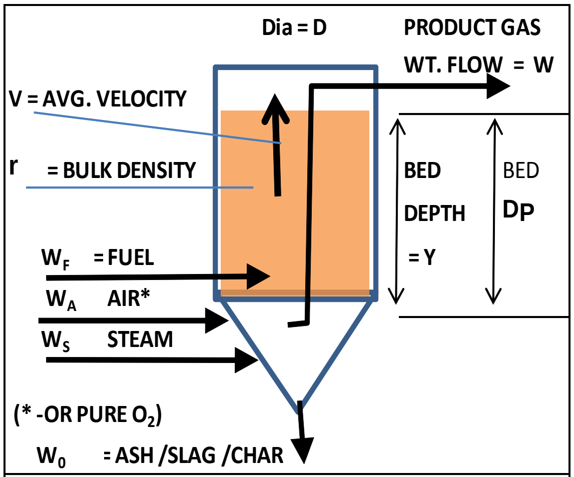
Throughput, W controlled by $(W_A + W_S)$

Temperature Variable, increasing from surface to combustion Temp. at bottom, controlled by W_A/W_F. Range of W limited by acceptable bottom Temp.

Composition ccontrolled by W_S/W_A

Feed rate, W_F, controlled to maintain bed depth, y.

FLUIDIZED BED



BED COMPLETELY, AT (ALMOST) UNIFORM REACTION TEMPERATURE, W/ ALL REACTIONS CONCURRENT.

$W = W_A + W_S + W_F - W_0$ Lb/hr

DP x Area must be ≥ Wt of bed, but --

V must be < V_E of near-smallest particles.

V_E = Entrainment Velocity, $= gd_2(r_p - r_g)/18m$

-- in consistent units.

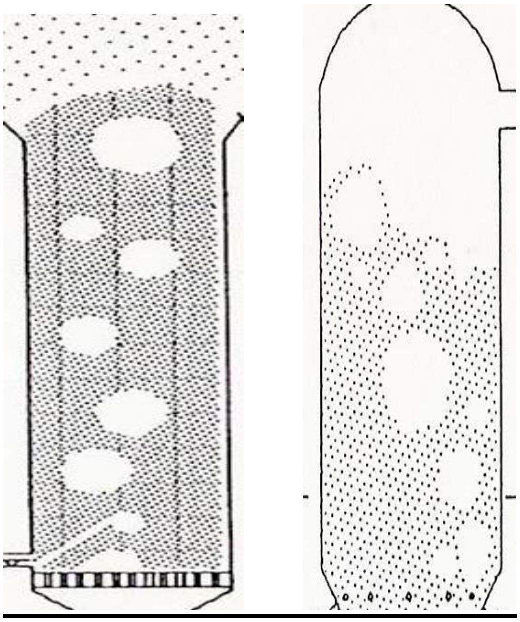
Approximate Viscosity of Air, CO, CO2, N2, CH4
m, lb/hr-ft = .0454 + .00005 x TºF All pressures.
(Lower for H2)

A major premise of the above designs is that the state of solid bed material will in fact be as defined and remain uniform. Material is free flowing and within a specified range of particle size and permeability. (Approaching the bottom of the material will break down into finer ash, but will remain free-flowing.) Throughput control of a fixed be gasifier is simply by adjusting the combined flow of steam and air or oxygen. The rate of solid feed simply follows the rate of consumption in the reaction zone. This design therefore offers very wide turn-down the upper limit on throughput is the gas flow or pressure drop that would lift the bed and allow blow-through. Bed temperature, where the different reactions occur, range from the maximum (combustion) at the bottom to a minimum (drying) at the top, where gasses disengage from the solid. This provides counter-current heat and mass transfer.

For a fluidized bed, the upward gas flow is constrained to the narrow range of proper fluidization, so the range turn-down ratio is quite limited. The overall thermal efficiency of the fluidized bed design is higher than the fixed bed, due to the higher particle surface areas available for reaction, because of the smaller particle sizes, plus more complete mixing of gas and solid. Average fluidized bed temperature is fairly uniform, but generally higher at the bottom, where maximum combustion takes place.

There are a few, less common, other kinds of gasifiers (entrained flow, spouting bed) that will be discussed in later sections.

Cold Simulation of Fluidized Bed to Select Proper Degree of Fluidization

V = Required volumetric flow to achieve visually selected pattern of fluidization. $V_1 = W_1 RT_1/M_1P_1$ = Flow, ft^3/sec at ambient conditions. W = Wt. flow, lb/sec. M1 = Mol.Wt. = 29 for air. V_2 = same, T2 ºR, actual P_2 lb./ft^2 & M_2 = Mol.Wt. of actual gas. Required: $V_1 = V_2$ $W_2 = W_1(T_1/T_2)(P_2/P_1)(M_2/M_1)$ = Required lb/sec at process conditions.	Glass or plastic, with same L/D ratio as real gasifier, filled w/ same bed material & feed. 

For feed preparation, all materials must be ground to some specified size. Feeds subject to brittle fracture, such as coal, minerals or hard plastics, such as PVC, and brittle biomasses, such as nut shells or pits, crushing, grinding (for fixed beds) and pulverization (for fluidized beds) can be accomplished by jaw crushers, hammer mills and tumbling ball or rod mills. All these are relatively cheap, compared with fibrous materials, such as wood and most municipal waste components that are not brittle and will need to be shredded, or finely ground in attrition mills, which have lower throughputs than hammer mills, and are thus more expensive. Waste tires must be clopped and shredded in several stages and are far more expensive to reduce to granular form.

Physical Properties

For the above major premises of bed design to apply in fact, the following properties must be taken into account.

BULK SHEAR STRENGTH OR ANGLE OF REPOSE.

These are measures of “free-flowingness,” or the ability of a material to slide against itself in motion. They are seldom actually measured and can usually be taken into account intuitively by engineers who have worked with them. Most brittle fracture materials of uniform size will settle freely sown silos, hoppers or reaction vessels. The slope of cone-bottom vessels must be greater than the angle of repose. Wood chips and chopped tires are not so free-flowing and may need wider vessels (in proportion to particle size) to avoid bridging, and some form of mechanical agitation (stirring) to keep flowing. Stringy, fibrous stiff, like shredded plastic film, corn stalks, straw or other wastes need to be continuously nudged long, such as by screw conveyors. In the case of fluidized beds, an inert be material, such as sand, is used to assure fluidity, with the sand occupying a larger volume of the vessel than the reacting material.

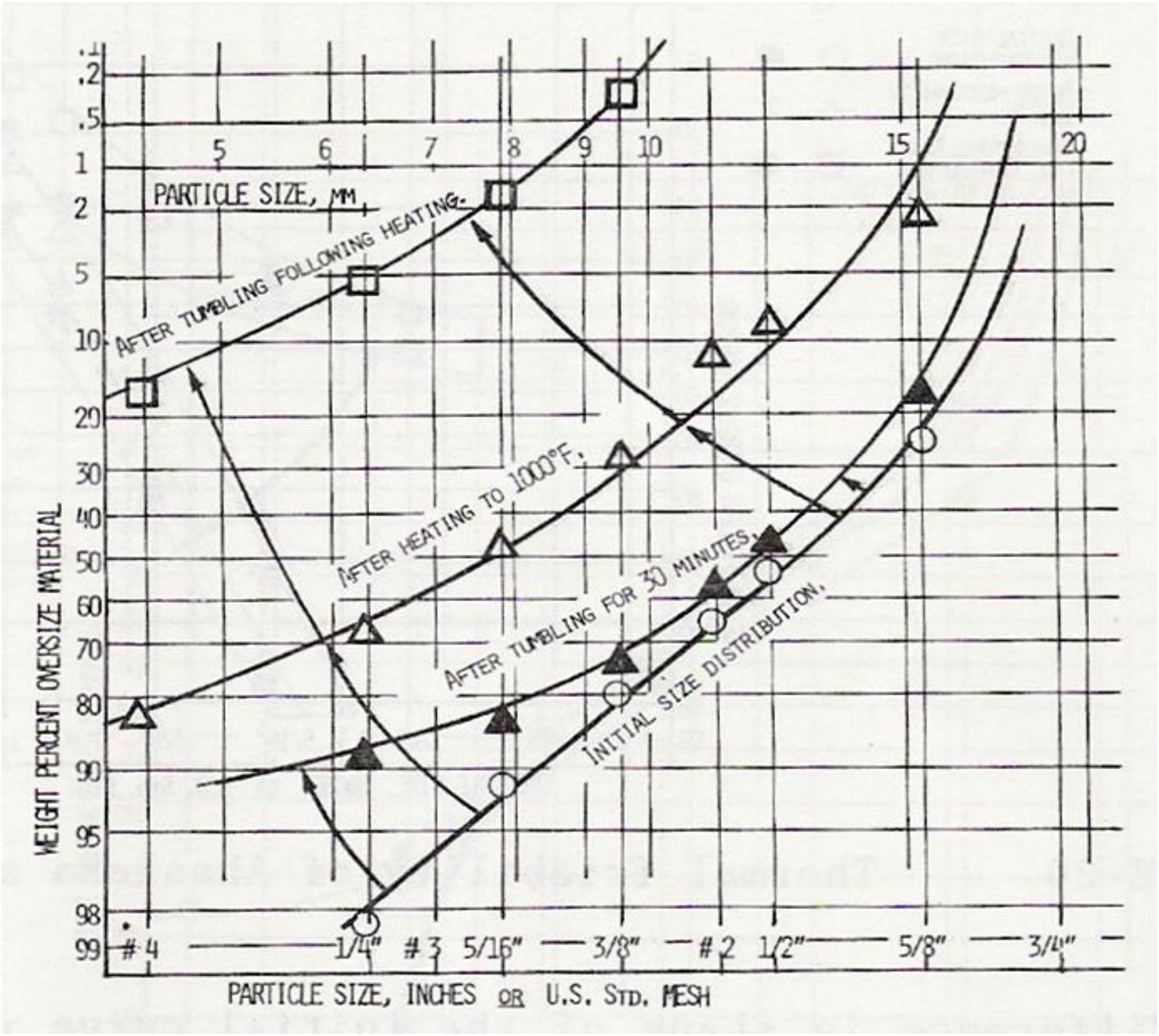
FRIABILITY – THERMAL & MECHANICAL

During gasification or pyrolysis, as feed particles are consumed, they may simply shrink, or they may become brittle and be ground finer by tumbling action, or simply disintegrate into dust. In any case, an accumulation of much finer particle size will affect permeability, fluidization and dust carry-over. As an example, lignite (German: Braunkohl. Australian or South African: Brown Coal) is a “low rank” coal (high ash and moisture content) generally preferred for gasification processes, in which tightly bonded moisture essentially holds the solid carbonaceous structure together. The following plots show what simply drying can do to particle size distribution of a typical lignite. (A few lignites that appear quite dry in appearance and to touch, may actually contain over 50% moisture.)

The lower line shows the material ground to 98% +1/4” as used in a series of pilot scale fixed bed, gasifier tests. The sample was then gentle tumbled for 30 minutes, after which sieve analysis showed it reduced to 88% +1/4”, with less change for the larger particles. Then an identical sample, with no tumbling was simply heated to 1000ºF, which shifted the entire size distribution curve upward, with only 68% remaining +1/4”. This sample was then tumbled for 30 minutes, with the thermally reduced friability, resulting in far more extreme disintegration, to only 5% remaining +1/4”. This tells us that to use this lignite in a fixed bed gasifier, the upward gas flow, and thus the production rate, must be kept relatively low, to avoid massive carry-over of fine, unreacted feed with the product stream.

Similarly, in a pyrolysis process for waste tires, shredded feed, at about ½’~ ¾”, was pyrolyzed in an externally heated horizontal reactor, to about 600ºC/1100ºF, moved along gently by a drag chain conveyor. Through a series of 5 production runs, 25.5~28.6 % of the raw feed was recovered as char, in a size range acceptable for conversion to activated carbon, while 5.5~15.4% was reported s fine dust, less useful as product.

Effect of Heating to 1000ºF on Friability of a Typical Lignite.



So far, we have addressed the necessity of feed particles being of the right size and free-flowing, and the problems particle disintegration to smaller sizes. As serious or more so, are the problems of particles agglomerating to larger sizes, usually accompanied by blocking the flow of gasses or sticking to walls of equipment. Of possible feedstocks, most coals, all rubbers, most plastics and – under certain conditions – some biomasses, will pass briefly through a sticky, heavy liquid phase, of high boiling points, on their way to complete pyrolysis to gas and char. (See Reaction (9) in “Chemistry,” above.)

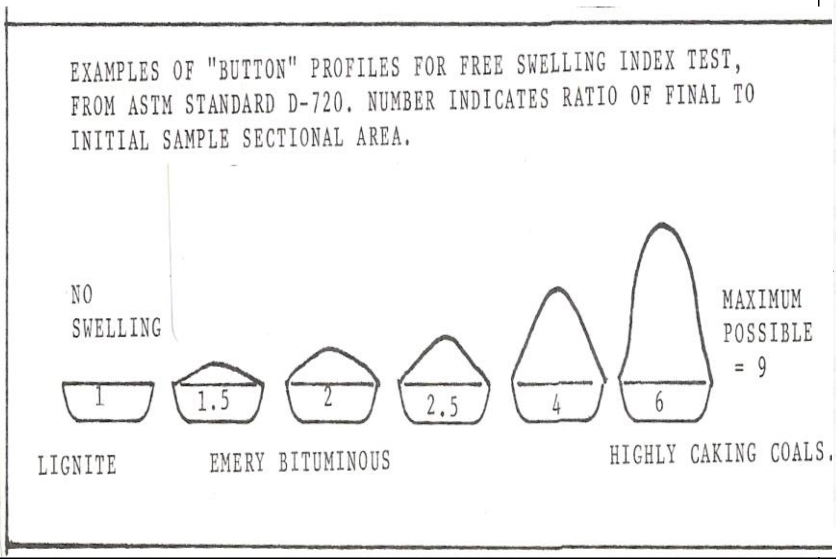
An established laboratory method for predicting this behavior in coal is the Free Swelling Index (ASTM Standard D-720) shown below. As the sample is heated, pyrolysis produces a viscous/gooey/tarry fluid, which is puffed up by released gasses, and continues to pyrolyze, fusing into a solid porous muffin-like button. Simple visual comparison of the button with the profiles shown gives the standard measurement of this property. Typical lignites have a FSI value of only 1 or 2. Subbituminous and bituminous coals show increasing values, up to possibly 9, for some bituminous “coking coals,” used to make metallurgical coke, for steel production. Among dry biomass materials, sawdust or finely chipped wood typically has a value of 1 or 2, while popcorn is probably at full-scale 9.

Standard Test for Free Swelling Index

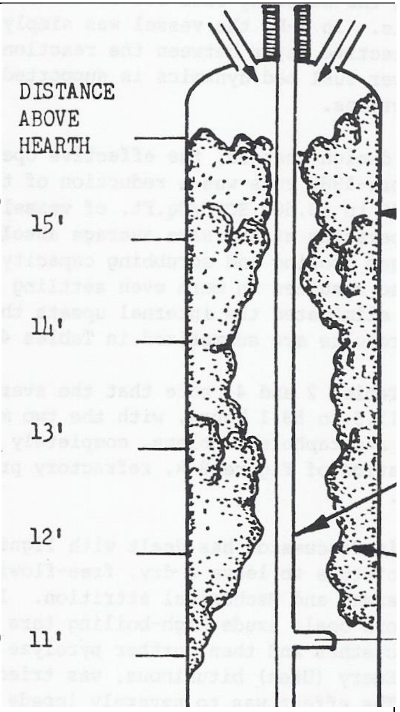
(1) Fill 1” crucible w/ ground sample

(2) Heat to 1500ºF w/o air.

(3) Match to standard. Profile, below.

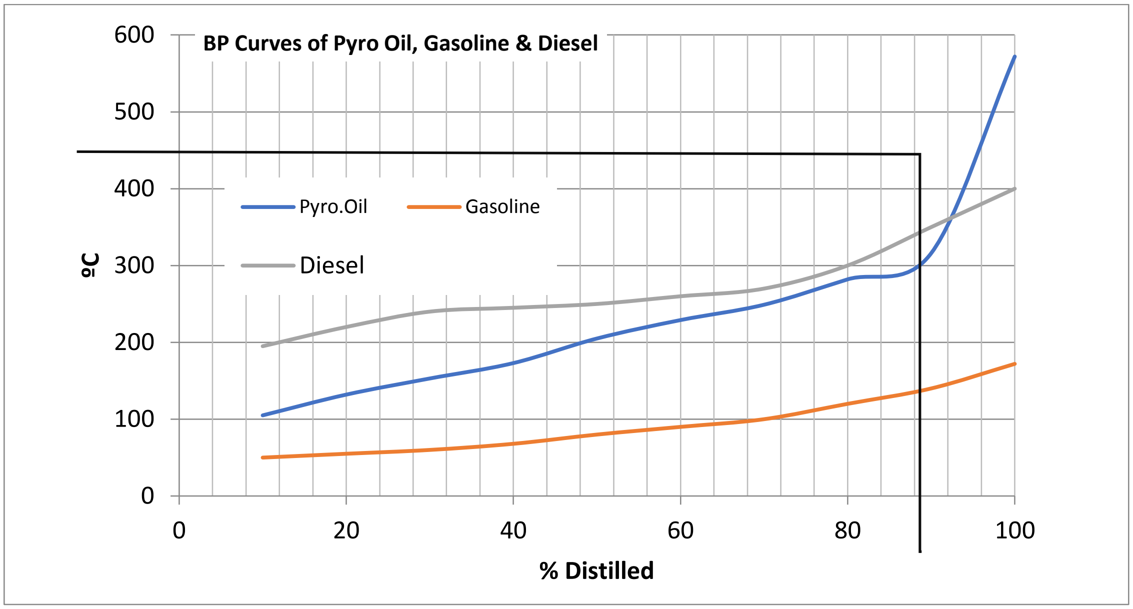


EXAMPLES OF "BUTTON" PROFILES FOR FREE SWELLING INDEX TEST, FROM ASTM STANDARD D-720. NUMBER INDICATES RATIO OF FINAL TO INITIAL SAMPLE SECTIONAL AREA.



The inserted sketch above shows the result of feeding a relatively high-FSI subbituminous coal to a pilot scale (24” diameter) fixed be gasifier. A stirrer was provided to keep the stuff free-flowing, at lower levels. However, pyrolysis and resulting agglomeration plugged up the unit at the top, as shown. (See “Worst Case Demonstration Unit,” later in this work.)

A similar phenomenon occurs in pyrolysis processes, when heavy, condensable vapors condense where they should not. For an example, a waste tire pyrolysis produced a heavy “pyro oil” product, compared with boiling point curves of gasoline and diesel, as shown below. In the reactor, a drag-chain conveyor moved the solid feed along the inner wall of a reactor vessel, heated to about 600ºC (1100ºF) by a surrounding furnace. Pyrolysis of the highest-BP components occurred in intimate contact, and temporary thermal equilibrium with the hot surface. The average temperature throughout the reactor vessel was about 450ºC (840ºF), based on the temperature of the exiting gas and vapor stream. Therefore, from the BP curve below, at 450ºC, about 97% of condensable products were sill safely in a vapor state, while the higher-boiling 3% would be condensed as a mist. These sticky droplets then adhered to suspended dust particles and to equipment surfaces up leaving the reactor. An otherwise successful production run lasted for about 90 days, at which time the reactor outlet piping became plugged and the process inoperable.



To this point, we have covered processes where any non-carbonaceous mineral matter remains as dry ash. But in all gasification processes where some part of the feed is burned to provide process heat, ash may be heated to its melting point or beyond, forming a molten slag. For any fixed bed gasifier or "dry bottom" gasifier, while high temperatures are desirable to accelerate reactions, the final mineral residue, the ash, must remain a free-flowing solid. To assure this, the critical property of the feed is the **Ash Fusion Temperature**, at which the lowest-melting mineral components start to melt, and stick to solid particles.

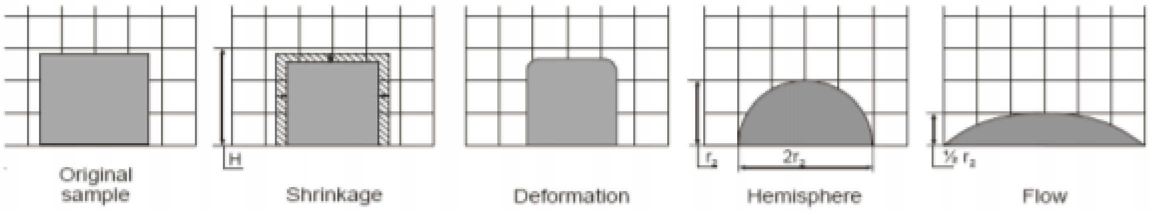
ASH FUSION TEST

The behavior of the coal's ash residue at high temperature is a critical factor in selecting coals for steam power generation. Most furnaces are designed to remove ash as a powdery residue. Coal which has ash that fuses into a hard glassy slag known as *clinker* is usually unsatisfactory in furnaces as it requires cleaning. However, furnaces can be designed to handle the clinker, generally by removing it as a molten liquid.

Ash fusion temperatures are determined by viewing a moulded specimen of the coal ash through an observation window in a high-temperature furnace. The ash, in the form of a cone, pyramid or cube, is heated steadily past 1000 °C to as high a temperature as possible, preferably 1,600 °C (2,910 °F). The following temperatures are recorded;

- *Deformation temperature*: This is reached when the corners of the mould first become rounded
- *Softening (sphere) temperature*: This is reached when the top of the mould takes on a spherical shape.
- *Hemisphere temperature*: This is reached when the entire mould takes on a hemisphere shape
- *Flow (fluid) temperature*: This is reached when the molten ash collapses to a flattened button on the furnace floor.

The appearance of these shapes is shown below.



The most important observation is the shrinkage temperature, which is where the lowest melting components begin to melt, and become an immediate threat to free flowing solids. This is therefore the **maximum temperature that should be avoided** at any point within a gasification vessel. For the test data above, this should be no higher than the shrinkage temperature, beyond which the test sample starts to become fluid and "sticky.'

The possible mineral content of coal is infinite in variety, determined only by that of the soil in which the original plant material was grown, and has no correlation with any other coal properties. This property applies to biomasses as well as coals. In biomasses, the ash is composed of relatively mobile elements in the plant tissues. These are mostly potassium and calcium carbonates. Most grassy materials, like straw and corn "stover" (stalks & leaves) have a substantial silica content. This is especially high in rice hulls, which are a choice, easily collected, free-flowing gasification feed, but with a high silica content, of which the softening point is the limiting factor in the maximum permissible temperature in the successful fluid bed gasifiers marketed for this purpose.

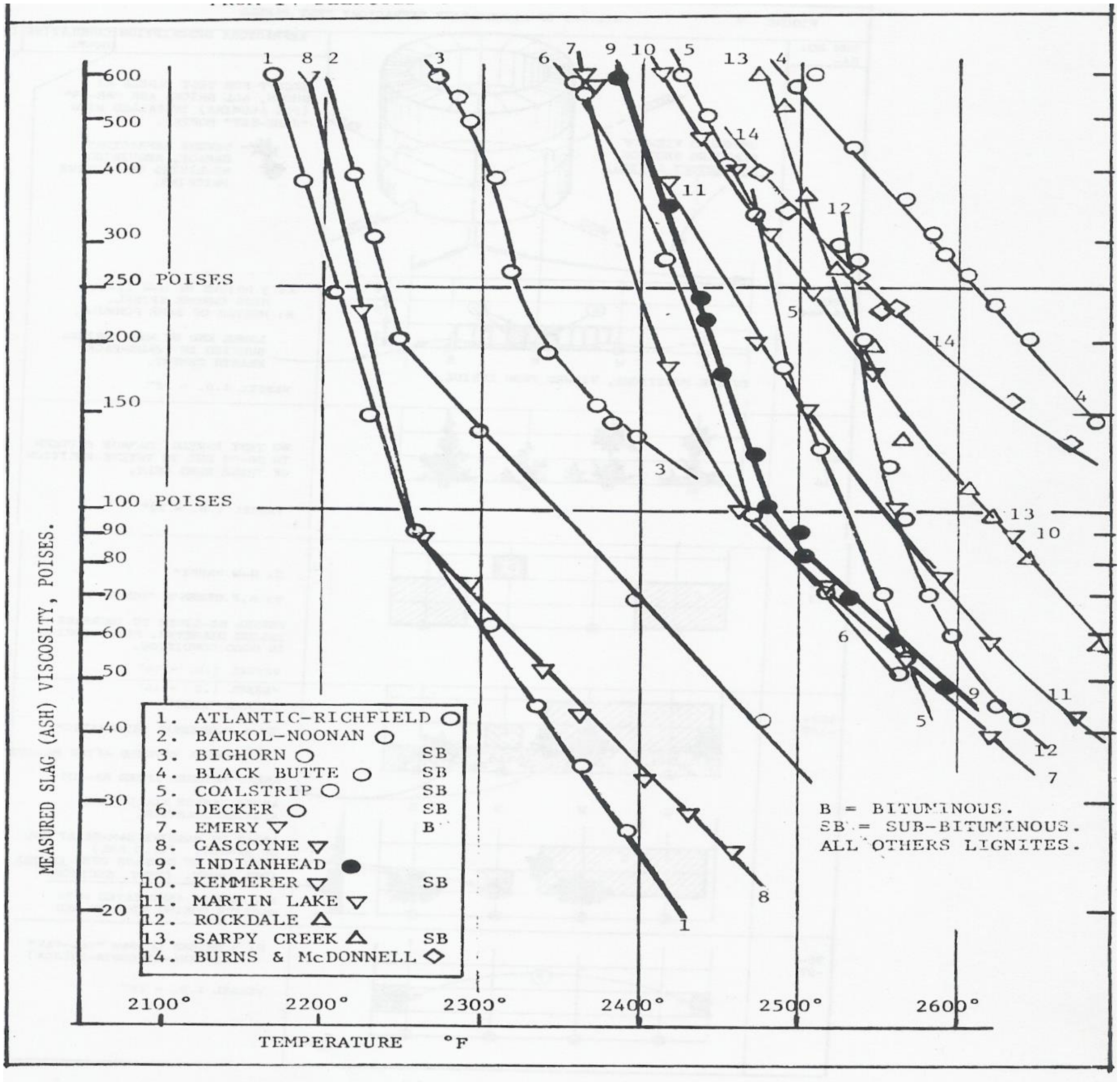
In the above illustration, the "flow temperature" is where almost all mineral components are completely liquid. For slagging gasifier designs, which operate at higher temperatures than "dry bottom" designs, where all ash is a liquid slag, this is an **absolute minimum temperature that must be avoided**.

SLAG VISCOSITY

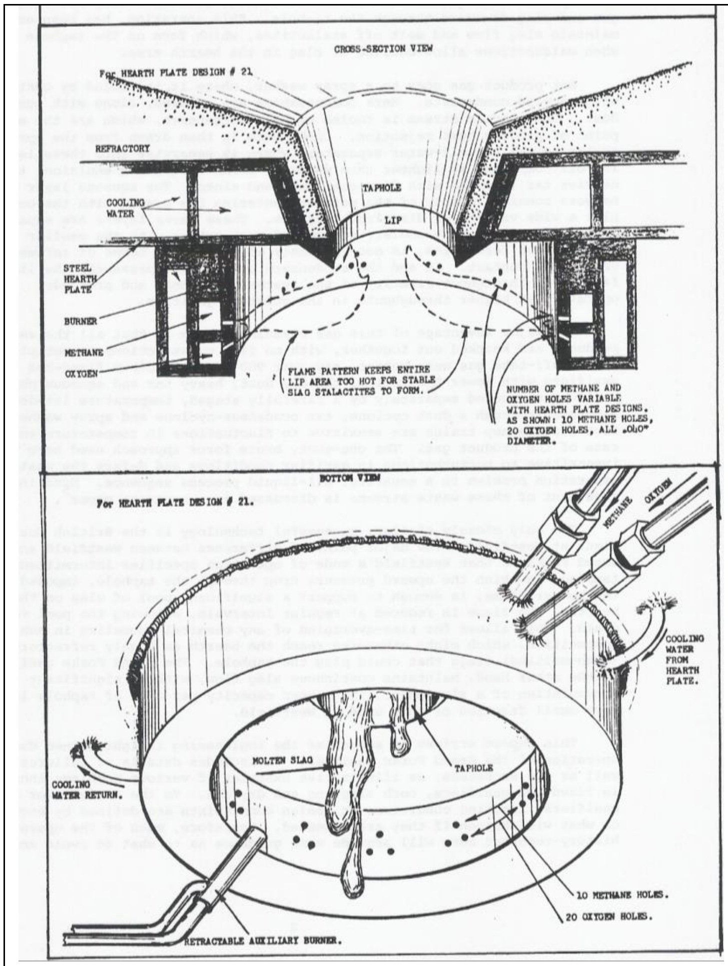
Slag viscosity is essential to slag flowability in high temperature processes.

Most established operational designs for coal gasifiers are dry bottom designs, requiring solid free-flowing or fine, gas born removal of residual ash. Others, the “next generation” large operational designs are slagging gasifiers, operating at temperatures well above the complete melting points of all mineral components, so that ash becomes a free-flowing slag leaving the reaction zone. For such applications, the slag viscosity is the key variable -the potential “show stopper”- dominating design problems.

Coal ash, as liquid slag, comes in an infinite variety of mineral compositions, all composed of multiple minerals of different melting points. These slags thus have wildly variable viscosities, which are steeply variable with temperature. Below is a plot of viscosity temperature curves for 16 different US coals that have been used or at least tested in full- or pilot-scale slagging gasifiers. This shows us that if we need a slag with maximum tolerable viscosity of say 100 poise or lower, the minimum temperature in the reactor vessel – or at least the lower levels where final separation of carbon and mineral matter occurs – we need to maintain a temperature of 2250^{o}F to 2550^{o}F for 14 of these coals, and probably as high as 3000^{o}F for 2 of them, From the point of initial melting, to the point of final separation of flowing slag from any solid surface into a water quench bath, the temperature must be maintained. Considering the steep slope of these curves at 100 poise, temperature control is critical.



As an example of this type of problem, below is an illustration of current problem with a pilot scale (about 1 Ton/hr coal feed) slagging gasifier, presented in detail later, as the WCDU (Worst Case Demo Unit) The coal used here is unknown, but most probably Indianhead lignite. (See viscosity plot above.) The required minimum viscosity was never known, but was reported as about 2400ºF, at the taphole, which would correspond to a viscosity of about 500 poise for this lignite. In this case, the unit was operated at 300psi, with temperature controlled to roughly 2000ºF at the gasification zone, a few feet higher, with a probable combustion zone temperature of possibly 3000ºF at 3 to 4” above the taphole. Temperature exactly at the tap hole was controlled -most of the time- by a ring burner just below it, as sketched, and under more desperate conditions, by the manually manipulated burner directed at it. When temperature at the taphole and hearth got too high, the refractory covering the hearth plate melted, exposing bare metal, which also melted. When the temperature got too low, slag solidified and the unit was shut down due to terminal constipation.



RECURRENT SLAG FLOW PROBLEM ENCOUNTERED IN THE GF SLAGGING GASIFIER DESIGN.

- Slag flow controlled by pressure drop across taphole.
- Slag heated by 2000ºF combustion zone against hearth and cooled by heat flow through refractory on hearth and taphole.
- Slag from taphole heated by ring burner to maintain fluidity.
- When slag starts to freeze, heat transfer from above is decreased and freezing rapidly accelerates.
- Manual auxiliary burner used to re-melt slag - or taphole plugs causing shut-down.
- If slag is too hot refractory on hearth plate is eroded, burning hole in water-cooled plate.

Ref.: "Conclusions of Slagging, Fixed-Bed Gasification of Lignite." By W.B.Hauserman. University of North Dakota Energy Research Center,

SLAG CHEMICAL REACTION WITH REFRACTORY SURFACES.

Molten slag, especially formed in the reducing atmosphere, of a gasification zone, can be powerful solvent for other minerals, such as those used to make refractory reactor linings. Reducing gases, at these high temperatures can cause partial reduction of metallic oxides, to completely unpredicted molecular species. Also, reduction of various ash minerals can release temporary, unstable compounds that in turn can react with the carefully engineered crystalline structures of high-temperature refractories, converting them fragile compounds that flake off from walls, becoming part of the slag.

SiO_2 + H2 → SiO + H_2O
Cr_2O_3 + 4H2 → 4 H_2O + 2CrO, which has a melting point of only 300ºC (570ºF)

Detailed analyses of decayed refractory linings and slag deposits from the WCDU were done, revealed a huge variety of these products. Complex sodium-aluminum-silicate minerals in the lignite ash can break down, releasing, for instance, Na2O, which, as a liquid at these temperatures, is a powerful solvent to dissolve other minerals, forming aluminosilicates that were not on the lignite ash. Zirconium, for instance, is a component of many very durable refractories, and simply not present in natural lignite ash. Analysis of some refractory ecay products revealed Zr2O/SiO_2/Al_2/O_3 ratios of 65/12/23. And a spot X-ray analysis (done by SEM, scanning electron microscope) revealed odd fern-leaf mineral with composition of 83% Zr_2O and 8% SiO_2. Following episodes of refractory loss from the above hearth plate, samples slag revealed solidified bubbles, masses of fibers (magnification 2000X) of these synthetic minerals. In one case, a solid stalactite formed by the solidified dripping stream sketched above, revealed significant amounts of Cr, Ti and Zr, for instance, leached from the refractory. In such cases, this artifact was a disturbing motley pink color, attributed to some chromium oxides, and referred to by operators as a “hemorrhoid.”

In summary, there is no rule of thumb for gasifier designers, regarding refractory selection, except to predict as nearly as possible the temperatures of flowing slag. Any design for a slagging gasifier must include a complete analysis of the ash mineral content, and involve the providers of the refractories to be selected.

4. Atmospheric Gasification for Power Generation or Process Heat

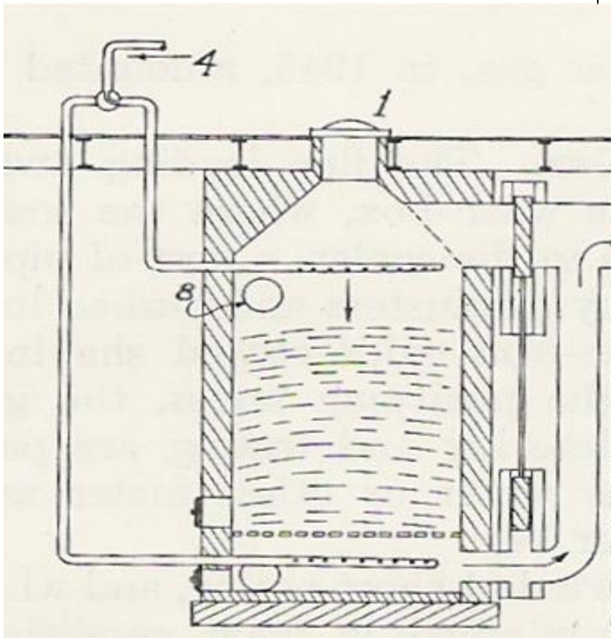
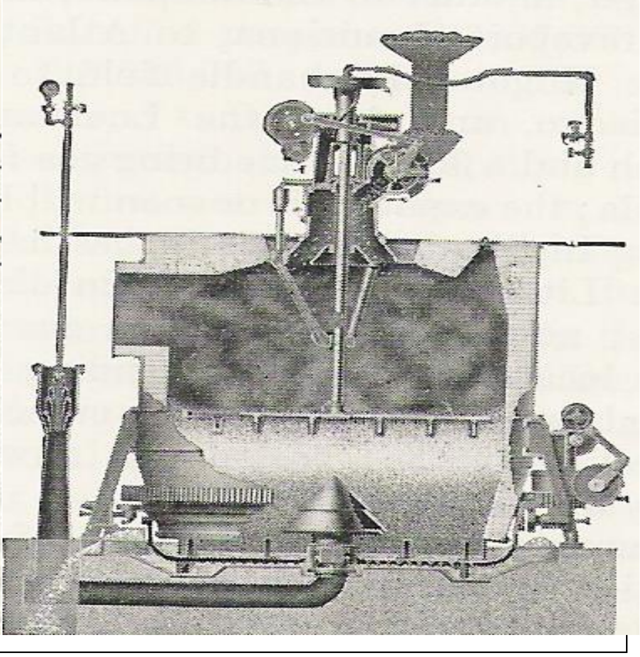
These are, chemically, the simplest of gasifier design concepts, offering providing maximum overall thermal efficiency, with minimum parasitic loads, like endothermic reactions or gas compression. They are all characterized as follows.

- Partial Combustion
- No steam injected
- Endothermic, steam-char reaction avoided, to maximize overall energy efficiency, defined as (Potential + Sensible Heat in Products) / (Potential Heat) in feed
- Volatile pyrolysis products thermally cracked and /or completely burned
- Gas may be used hot, directly to closely coupled boiler, or may be cooled and filtered or scrubbed, for use an engine-generator set
- Low-Btu product (high N_2) gas at ambient pressure
- Actual Efficiencies not readily published, but cab be quite high, determined mainly by heat losses, rather than chemistry
- Air pre-heated by recovered boiler or engine exhaust heat, for greater efficiency. Heat recovery is major factor determining efficiency.
- Used mainly for biomass and wastes

Some example processes are described below, starting with the historically earliest, relatively primitive. Websites are given, for specific providers, as sources of more information.

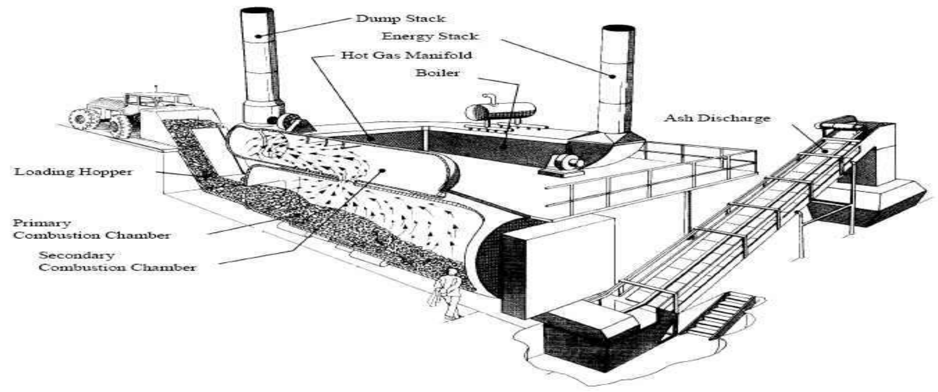
Below are shown early examples of “Water Gas” or “Town Gas” Generators:

- Using Partial Combustion plus Steam Gasification.
- Widely used commercially in years 1890~1920.
- Product: 150~300 Btu/SCF (Compare natural gas: 1100 Btu/SCF)
- Operation: Cyclical. Coal intermittently burned (Reactions 1 and 3), then quenched with water spray (Reaction 4).

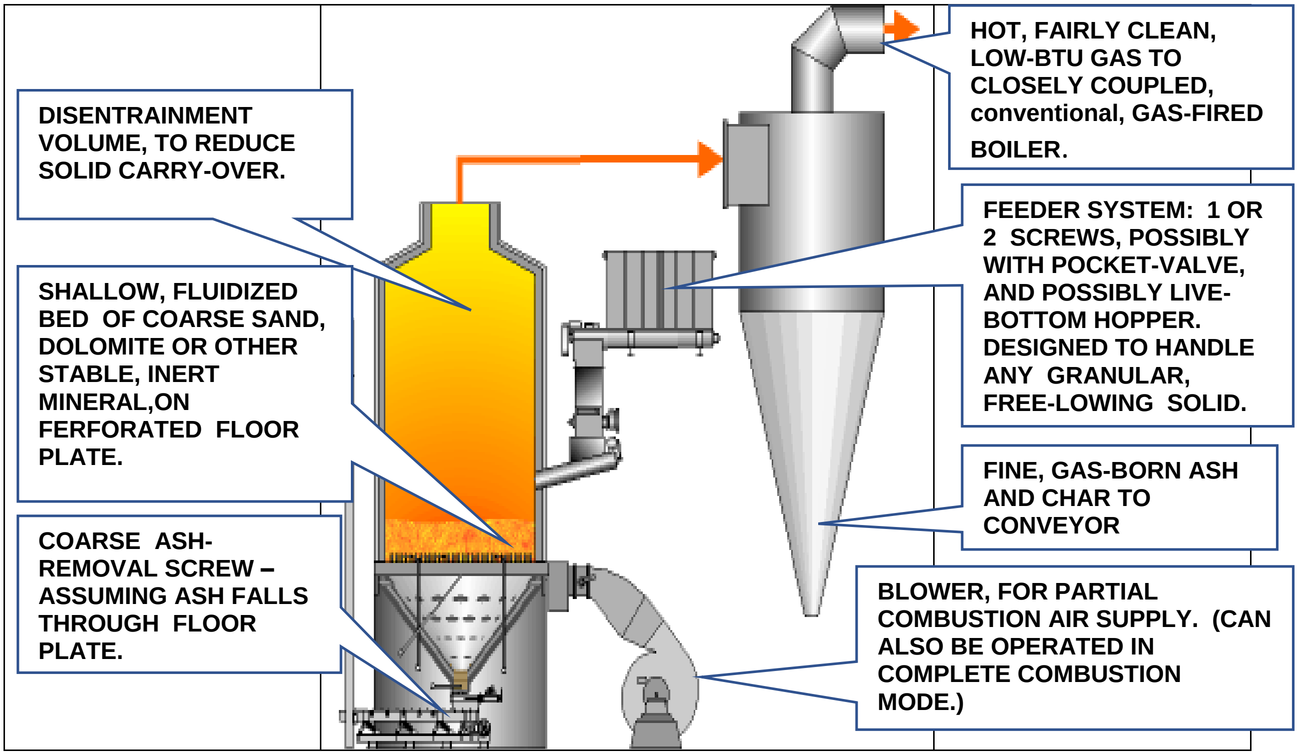
Water sprayed on incandescent coke. Cycles 5~7 minutes, 2550ºF to 1830ºF. Typ. 10 ft dia. X 15 ft tall. Proportions: 1- Coal 4-Steam 6-Air	Chapman “Modern Gas Producer” 10 ft dia. X 12 ft tall. Coal: 3000 ~ 4000 Lb/h Continuous Air/Steam: 7/1 Volume Steam/Coal: 0.25 ~ 0.5 Weight.
	

Gasifiers like this were once used to provide gas domestic cooking and heating, and for street lighting. Their product consisted of mostly CO and H_2, and small amounts of CH_4. The CO caused a then-accepted domestic health hazard. These were made obsolete by general availability of natural gas.

As an alternative to highly polluting combustion of municipal waste (garbage), which require archaic moving grate or other solid fired boilers to produce electricity. Gasification can offer a fuel gas, capable of being cleaned up – (pollutants removed) - for use in gas-fired boilers. Below is such a fairly primitive but effective “controlled air combustion process” to consume processed (sorted and ground) refuse to produce electricity. Solid feed is moved through a primary combustion chamber by a drag chain or moving grate with possible carry-over to secondary chamber, where solids can settle. Many of these are still in operation, with minor improvements.



A more advanced concept is the simple fluidized-bed gasifier for partial combustion (no steam-char reaction) to supply heat to a conventional gas-fired boiler. The specific example shown has been successfully used worldwide to process rice hulls, a neat, uniform, free-flowing, high energy solid fuel. The design has also been successfully tested and used with pre-processed municipal garbage (also called RDF – Refuse Derived Fuel). The reactor bed is a bed of carefully graded sand, to provide uniform turbulence and distribution of the feed, as well as thermal momentum, to assure uniform temperature. Sand that escapees the bed with coarse ash is recovered by sieving and or air separation and recycled.



DISENTRAINMENT VOLUME, TO REDUCE SOLID CARRY-OVER.

SHALLOW, FLUIDIZED BED OF COARSE SAND, DOLOMITE OR OTHER STABLE, INERT MINERAL,ON FERFORATED FLOOR PLATE.

COARSE ASH-REMOVAL SCREW – ASSUMING ASH FALLS THROUGH FLOOR PLATE.

HOT, FAIRLY CLEAN, LOW-BTU GAS TO CLOSELY COUPLED, conventional, GAS-FIRED BOILER.

FEEDER SYSTEM: 1 OR 2 SCREWS, POSSIBLY WITH POCKET-VALVE, AND POSSIBLY LIVE-BOTTOM HOPPER. DESIGNED TO HANDLE ANY GRANULAR, FREE-LOWING SOLID.

FINE, GAS-BORN ASH AND CHAR TO CONVEYOR

BLOWER, FOR PARTIAL COMBUSTION AIR SUPPLY. (CAN ALSO BE OPERATED IN COMPLETE COMBUSTION MODE.)

Ref:. www.primenergy.com

The advantages of a fluidized bed gasifier over the previous fixed bed designs are –

- More uniform permeability, and thus more uniform reaction rates.
- Faster reactions, to enable smaller reactor size.
- More uniform temperature control.

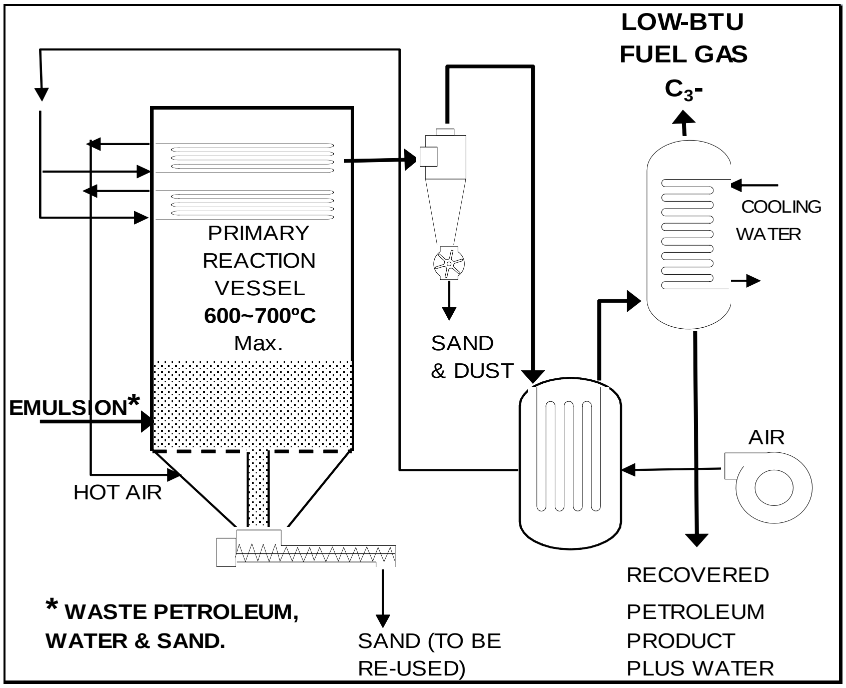
The trade-offs are –

- Limited turn-down range. Upward flow if gasses must stay within range to maintain fluidization. If too low, the bed settle/collapses. If too high sand blow-over with ash happens.
- Higher pressure drop and blower power are required. Pressure drop must equal the weight of sand.
- Requires more carefully ground and graded feed, to avoid oversized or extremely overweight particles.

A case study: The city of Sacramento, in the 1980s, established a curbside pickup of mostly yard waste, in plastic bags. These were taken to a steam plant in the middle of the city and fed to a gasifier similar to the one above. At one point, all the collected refuse was successfully consumed, except for the polyethylene bags, which, upon initial pyrolysis, formed sticky, high-boiling droplets that agglomerated into large carbonaceous masses, including nails from wood waste and other heavy non-combustibles that sank to the perforated floor being bypassed by the air and not consumed. (When visited, the plant was shut down. I never heard how this problem was solved.) Lessons for designers: (1) Remember that uniformity of particle size and thus permeability are critical. (2) Beware of unexpected agglomeration property of even minor feed components.

Ref.: http://powereng.com/RenewableDocs/Pat%20Travis%20%20Recycling%20Power%20Plants.pdf

A minor variant of the above up-draft, fluidized be design is its application to liquid wastes. Below is a simple fluidized reactor for gasification or combustion or pyrolysis of oilfield wastes for recovery of marketable petroleum fractions or process heat for other purposes such as brine evaporation.



Oilfield waste puddles, containing emulsions of crude oil, water sand and sometimes drilling fluids, are significant environmental pollutant sand impossible to reclaim. Where the crude oil content is high enough its heating value is enough to vaporize all the petroleum and water, and provide for gasification of the heaviest residues. This in effect distills the lighter petroleum fractions and provides a lot of useful heat. There are many such waste sites around oilfields that meet this requirement.

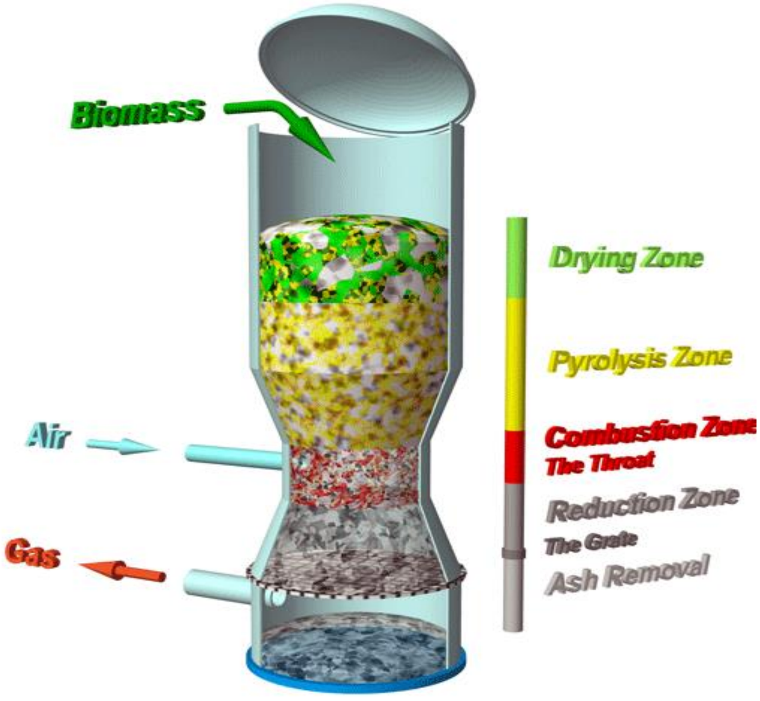
Ref.: www.operadoraintergrupo.com

The gasses leaving the reactor may consist mostly of superheated steam. This heat is recoverable by condensation, while preheating combustion air to the reactor, leaving a stream of fairly high energy fuel gas. A unit tested in Vera Cruz state of Mexico consumed 70 kg/h of an emulsion of 50% crude oil, 30% water and 20% sand, which delivered an impressive stream of recovered oil, resembling a light crude. This process is simple and well-suited to remote sites, where such waste deposits are found. It is also applicable to liquid wastes from pulp mills, which contain useful chemicals to be recycled from the ash.

This application could also be classified as steam gasification, with water in the slurry/emulsion feed supplying the steam. It could also be classified as a pyrolysis process, in that the valued product was simply distilled from the feed mix, rather than formed by gasification or other reactions. For a feed with a high petroleum content, the recovered oil could be a more valuable product than process heat, in which case one could reduce air flow, to burn only enough of the oil to pyrolyze / distill the rest.

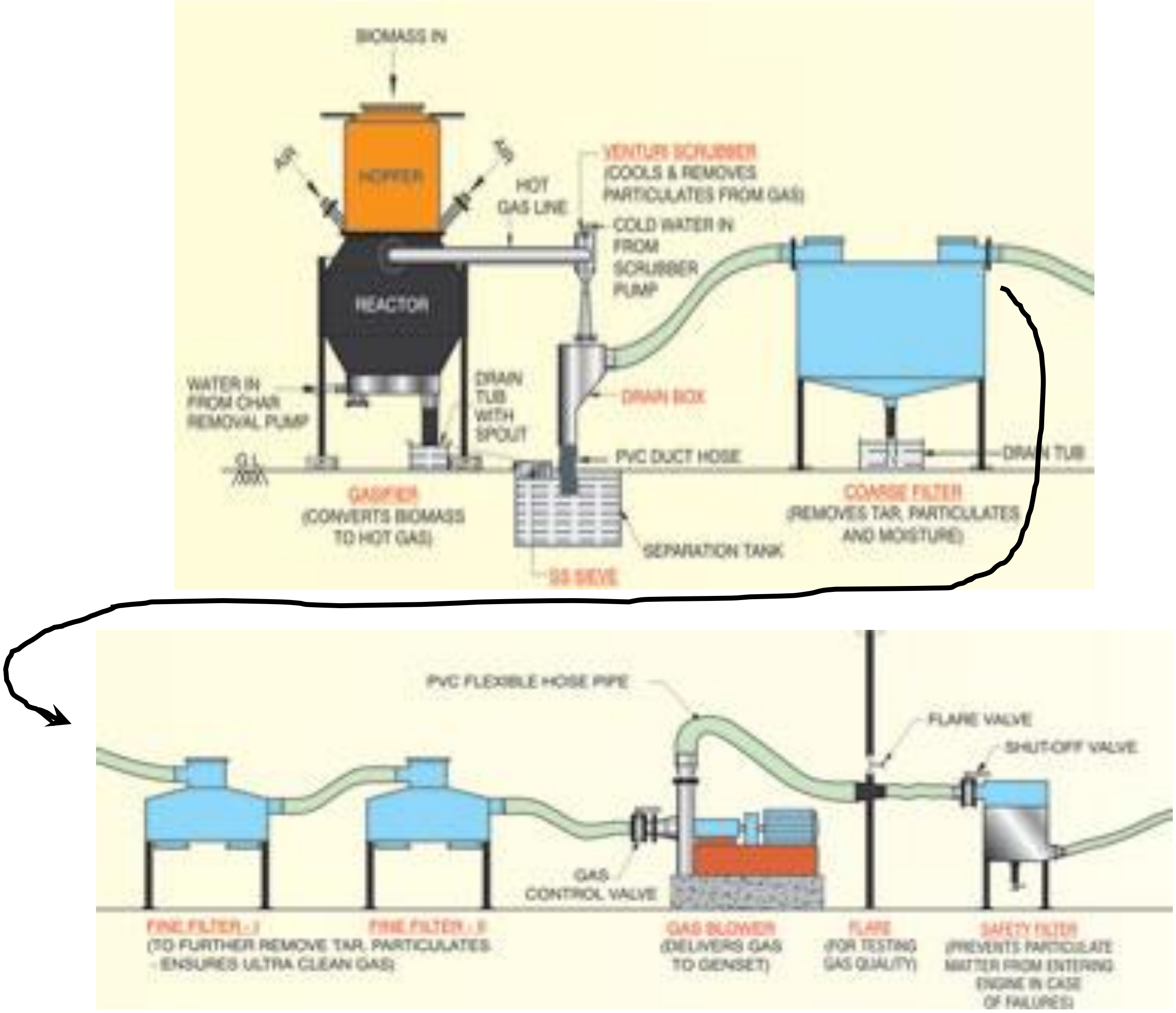
Note that this is a relatively deep fluidized bed, with feed inserted below the surface, as compared to preceding shallow bed, with feed inserted onto the top of the bed, from above. The advantages of a deep fluidized bed are certainty of immersion of solid or liquid feed into the bed, for more uniform temperature control, and longer residence time for larger or slower-pyrolyzing particles. The trade-off for this is a higher pressure drop is required, due to heavier bed. This process may be available commercially.

Another simple design is the Down Draft fixed bed gasifier, shown below. Here a wide variety of feed materials can be fed to the open top reaction vessel, where they settle by gravity and are slowly consumed from the bottom by a combustion zone. Where air is injected for partial combustion and product gases are drawn of by a slight vacuum from the bottom, with ash settling thru a grate. The settling feed is dried and pyrolyzed by heat permeating upward a short distance from the combustion zone. A wide variety of coarse feeds can be simply shoveled into the open top, from where some air is drawn downward by the applied vacuum, applied by a downstream suction blower.

A PRIMITIVE “CONTROLLED AIR COMBUSTION PROCESS” TO CONSUME PROCESSED (SORTED AND GROUND) REFUSE TO PRODUCE ELECTRICITY **TYPICAL GAS COMPOSITIONS, FROM RICE HULLS, COCONUT SHELLS, AND VARIOUS WOODY BIOMASS FEEDS.** CO 15 ~ 20% H_2 10 ~ 20% CH_4 Up to 4% CO_2 8 ~ 12% Calorific value 1050 ` 1100 Kcal/Nm^3 (123 Btu/SCF) Yields 2 ~2.5 Nm^3/kg Standard Systems Offered: Up to 858 kw Electrical Up to 2.2 Mcal/h (8.712 MBtu/h)	GENERIC DESIGN OF “ANKUR” GASIFIER, FOR GAS TO- • GAS ENGINE ELECTRICAL GENERATORS. • DUAL FUEL (GAS +DIESEL) ELECTRICAL GENERATORS. • THERMAL/DRYING APPLICATIONS 

Ref.: www.ankurscientific.com

This design is manufactured in India, with gas filtered and consumed by small gas or diesel generators, as shown below. Many such units in successful operation in India and other developing countries, providing minimal electric service to villages and remote locations where no electric power grid is available. These are manually loaded, with various agricultural wastes that need not be meticulously sized.



A power generator set (not shown) may be a gas engine or a diesel engine operating in the dual-fuel mode. In the later, a diesel can suck in variable amounts of combustible gases/vapors with its air intake, and will ct back of diesel fuel consumption, replacing up to 70% of its purchased fuel supply by gas from the gasifier. This offers the advantage of using diesel fuel as backup, to compensate for variation in or absence of available agricultural or industrial waste. For either kind of engine, a critical factor is that the gas must be completely clean – free of dust. For very low-cost applications, the gas could be used for gas lighting, thus avoiding the engine-generator and gas cleaning equipment.

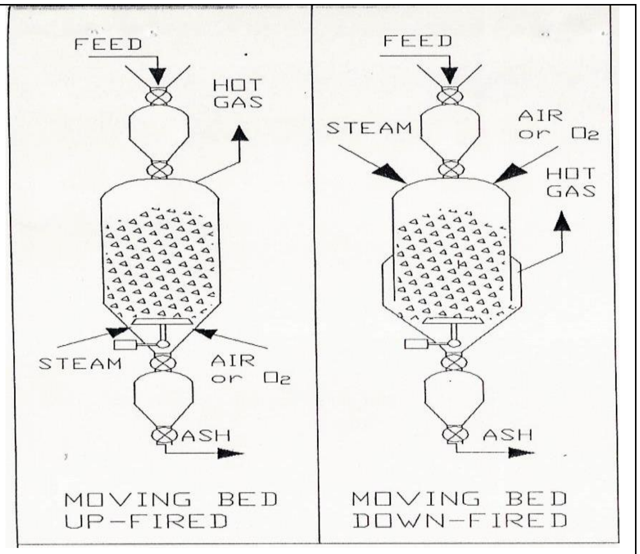
This design is widely used, world-wide, for small scale agricultural and industrial locations, to provide cheap gas for heating and drying operations. It is probably the most common approach used in many home-made gasifiers for such farm and light industry applications.

Advantages.

- Cheap.
- Accepts wide variety of solid fuels.
- Small scale and remote installations.
- Good for back-up or supplementary power.

Disadvantages.

- Requires continuous on-site personal attendance.
- Wide variation in gas quality.

Here is a generic comparison of up-fired and down-fired fixed bed gasifier designs, assuming pressurized operation, with lock hoppers for getting feed in and ash out. To function, lock hoppers require free-flowing solids, such as coal, or hard waste plastic (PVC). For less free flowing materials, like uniform chipped waste tires, some form of agitator in the lock hoppers are sometimes used to prevent bridging. Though a bit beyond the scope of this course, design of solid feeders is a major recurrent challenge in any pressurized gasification system.	

Most of the continuously operating gasifiers in existence are small units used for various biomass applications. Most of them are fixed bed, atmospheric designs, either up-fired or, more probably down-fired. These come in many design variants, many of which are home-made or offered by small, low-budget, low sales providers. They tend to be semi-custom designs, without any development subsidies, with no published data.

Fewer of these small-scale operations are fluidized bed designs, mainly because they require more careful control, have narrower operating range (turn-down ratio) and require more blower power.

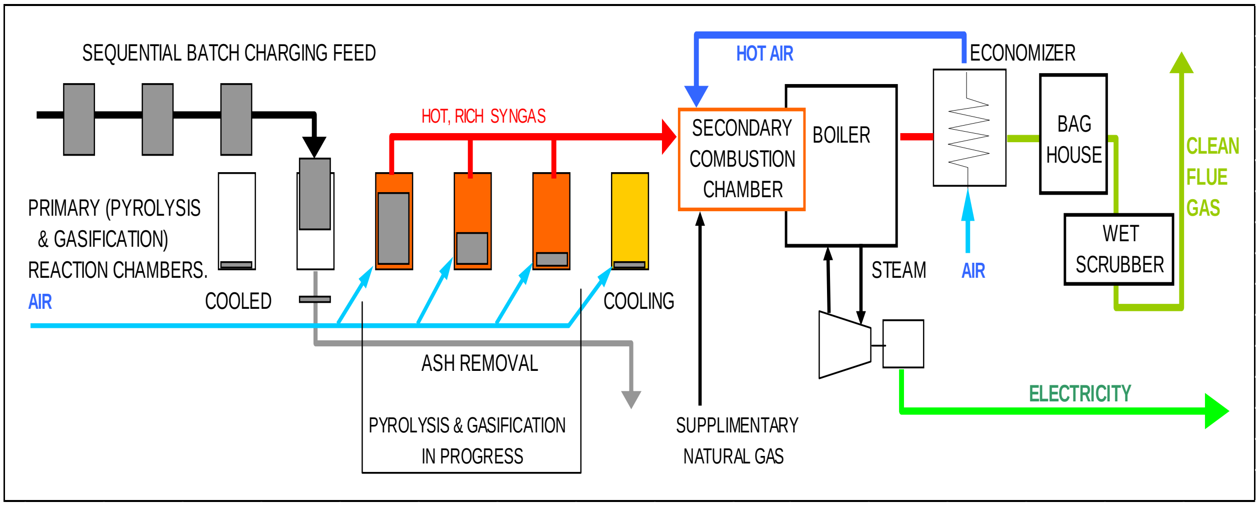
Successful coal gasifiers are all large scale operations, because coal is available in very large single-point sources (mines). This enables, or even requires, large investments to achieve the advantages of large scale, thus enabling more complex or advanced technologies. This is in contrast to biomass, which is usually available only from relatively smaller point sources, or would need to be collected/concentrated from large areas, with prohibitive transportation costs.

All of the above are continuous processes. Batch gasification is rare because the product gas supply is only intermittent and quality/composition highly variable with time. But a batch process can offer advantages for specific applications. The following example is probably the only medium-to-large-scale, completely omnivorous gasifier that can consume anything, with no grinding, shredding or other feed preparation required.

A SIMPLE EFFICIENT NON-POLLUTING WASTE GASIFICATION SYSTEM FOR ELECTRIC POWER PRODUCTION: EnEco TOPS™ (Thermal Oxidation Process System)

Sequential batch cycling of stationary bed batch gasifiers. Advantage: Can handle any feed, without grinding (including whole waste tires) for easy recovery of non-combustible recyclables.

Largest system in commercial operation (2010): 450 Tons/day of Municipal Refuse.



Ref.: www.eneco.ca

These reactors are large, rectangular sealed steel “closets” wherein any kind of refuse is rammed in, sealed, and ignited, with an air supply to provide partial combustion and limited gasification, depending on moisture content of feed. For hard to ignite feeds, such as tires or biological (slaughterhouse) waste, some supplementary fuel may be needed – such as diesel fuel or cellulosic (high-paper) garbage – may be needed. This combustion step is maintained until all carbonaceous material is consumed. The chamber is then opened, and all metal, glass or mineral residues are then pushed out, along with ash, completely intact, available for sorting and recycling. By having a sequence of such reactors operating in series, the blended gas stream is of acceptable uniformity. This stream then goes to a large, turbulent, secondary combustion chamber, with excess air, where all CO and potentially polluting pyrolysis products are completely and cleanly burned, providing heat to a conventional, otherwise-gas-fired boiler for power generation. This process is especially well-suited to specific industrial wastes that would highly polluting if simply burned, as well as to coarse municipal refuse, including furniture and appliances. It is also used for special, toxic wastes for which additional gas cleaning steps may be added. (Conceivably, it could even offer cremation services.)

The use of Municipal Solid Waste (MSW / Garbage) as falsifier feed is especially challenging, because of its very wide and erratically variable composition. Below is a table, prepared by the USEPA, in about 2000, showing the statistically average composition of all US MSW. It can be called the most probable US Official National Garbage composition, with the understanding that it will vary substantially between communities, and even between truckloads. As feed to a gasifier, or even to a conventional incinerator power plant, it should be ground and sifted to a uniform composition.

Composition	As Received.	Dry Basis	HHV (CV) kcal/kg	HHV by Components		Ren bota HH
Moisture (Nominal)*	20,00%					
Paper, newsprint	9,00%	11,10%	3998	444		444
Cardboard/corrugated	9,00%	11,10%	4047	449		449
Magazines	5,00%	6,20%	3572	221		221
Wood	7,03%	8,70%	4386	382		382
Rubber & Leather	2,50%	3,10%	5219	162		
Textiles	3,42%	4,20%	4199	176		
Plastic (Low density)	7,00%	8,60%	6969	599		
Plastic (High density)	4,52%	5,60%	6969	390		
Yard/Plant waste.	5,00%	6,20%	2203	137		137
Food/Kitchen waste.	7,50%	9,30%	2350	219		219
Other misc. organics	3,92%	4,80%	4391	211		
Glass/pottery	5,10%	6,30%				
Steel (tinned) cams	3,00%	3,70%				
Aluminum	4,00%	4,90%				
Other misc. inorganics	5,00%	6,20%				
Totals				3390		185

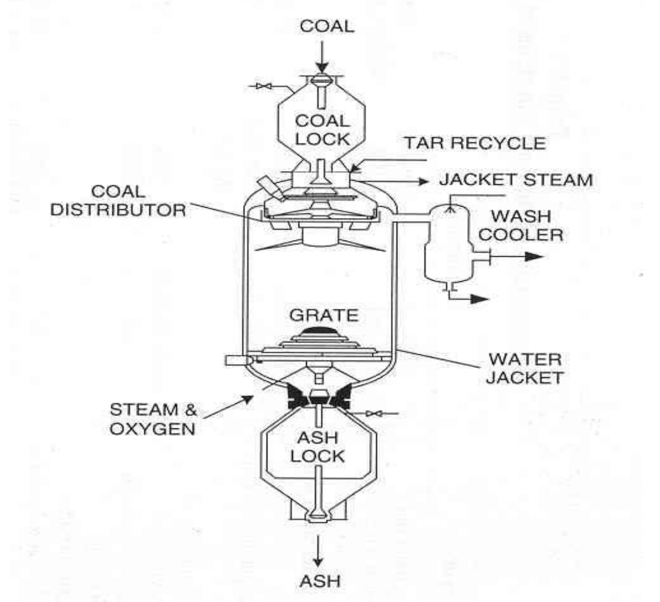
5. Pressurized Gasification with Steam and Pure Oxygen for Synthesis of Other Products

Graduating from the earlier and relatively primitive gasification designs, covered above in Section 4, we shall now consider more sophisticated technologies, involving the following:

- High pressures, from 150 psig to 300 psig and beyond, to provide the pressure needed for various downstream synthesis reactions.
- Use of steam, as the primary reactant, to produce high-btu gases, usually with maximum hydrogen content.
- Use of pure oxygen, rather than air, as the combustion agent, to avoid nitrogen dilution, for higher-btu products and smaller reactor volumes.

“Syngas” is any mixture of H2 and CO is so named because it can be used for the synthesis of a huge variety of other products. For this use the objective of overall thermal efficiency or maximum Btu delivery, is compromised by the requirement of a specific H2/CO ratio for the intended application.

Consider next, a specific application: SNG (Synthetic Natural Gas) produced by the reaction $3H_2$ + CO ↔ CH4 + CO2 + Heat. This is a catalyzed reaction requiring a high purity stream with an H2/CO ratio of 3.0. This case uses probably the simplest gasifier for reliable large scale operation – the Lurgi Mark 2 gasifier, developed and used commercially on a very large scale by Sasol, the national energy company of South Africa. Sasol has the capacity to produce somewhere over half of South Africa’s total gasoline and diesel consumption, produced by Fischer-Tropsch synthesis, defined later in this work, using syngas from these gasifiers.



- **F**ixed **B**ed **D**ry **B**ottom
- Counter current flow: coal down, agent and gas up
- Coarser coal: 5 to 100 mm
- Non-caking coals
- Limited tolerance to fines
- Long residence time (40-80 min)
- Ash content: 5 to 40%+
- Ash: non-melting, dry removal
- Ash melting point>1200ºC

Operated by Sasol, in RSA and

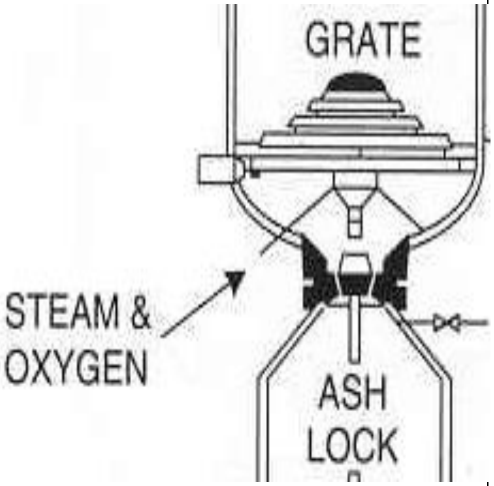
Others, operating and planned in China

Ref.: Dakota Gasification Company, ND USA.

Performance specifications for one of 12 Lurgi Mark 1V gasifiers at Beulah, ND as designed before start-up (early 1980s) – based on similar design developed at Sasol in RSA for liquid fuel synthesis.

INSIDE (WORKING) DIAMETER	**14 ft**	
OPERATING PRESSURE, psig	**430**	**300**
SPECIFIC GAS PRODUCTION: SCFH/FT^2 Cross-section	**11,037**	**7,800**
TOTAL GAS PRODUCTION : SCFH	**1,700,000**	**1,200,000**
STEAM CONSUMPTION, Lb/1000 SCF GAS	**55.8**	
O_2/SSTEAM MOL RATIO	**0.117**	
O_2 FEED, SCF/Lb COAL	**2.43**	
COLD GAS EFFICIENCY	**73%**	
WASTEWATER, Gal/1000 SCF GAS	**5.8**	
PRODUCT GAS, DRY BASIS		
H_2	**38.8**	
CO	**15.6**	
CH_4	**10.8**	
CO_2	**22.6**	
AVG. COAL USE, TON/h	**48.5**	

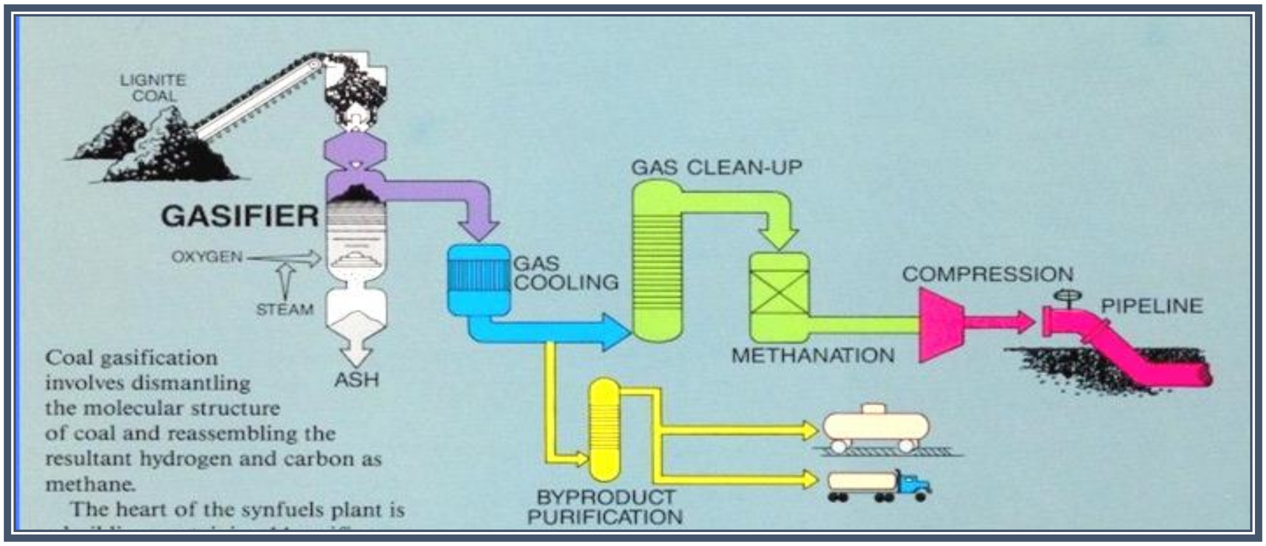
Detail of rotating grate to drop ash into lock. Steam and O_2 pass upward through grate



Below is a dimple flowsheet showing the overall function of the plant. It was built in the 1970s, in anticipation of an impending natural gas shortage – which hasn’t happened – yet. The plant has diversified and is currently using the syngas to synthesize a wider variety of chemical products. It is probably the most commercially developed and reliable design for large scale gasifies. Operating onus lignite and South African Brown Coal (Same stuff) it presents essentially no problems. The eccentric rotating grate at the bottom of the reactor serves to slowly alter support for the reacting bed of coal, thus weakening any bridge (discussed below) or other non-settling structure that may develop.

Depending on variation in the coal feed, and the steam/oxygen ratio, this gasifier a yield of syngas equal to roughly 180% of the feed, on an MAF (Moisture and Ash Free) basis.

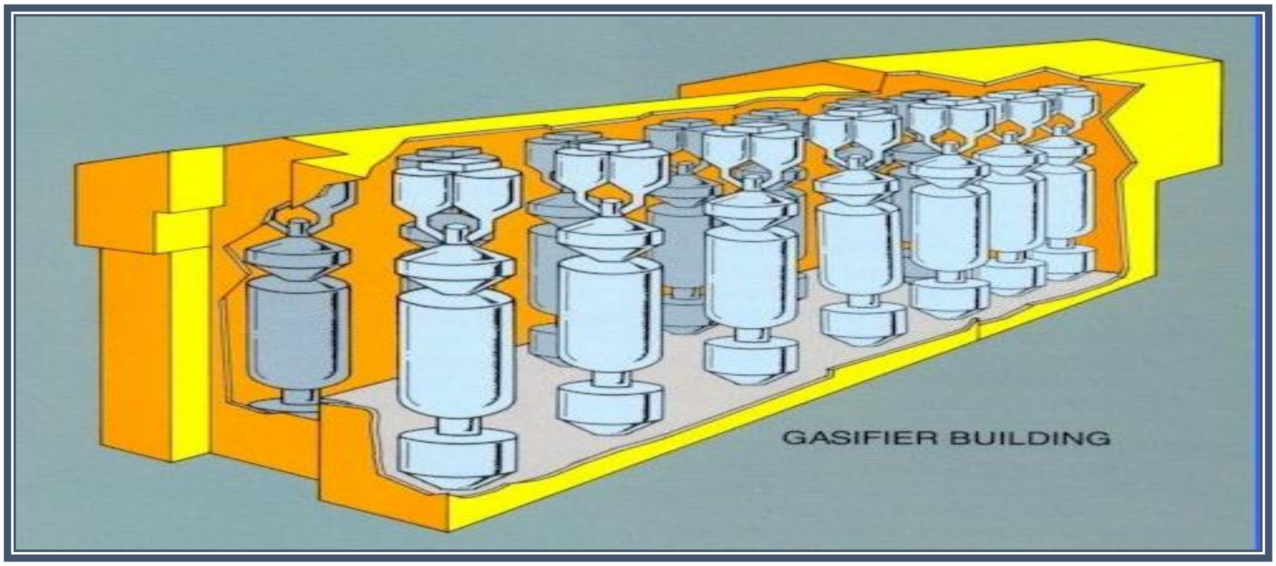
Along with this comes 2~3% of feed as noxious soluble organics and 3~4% as oils/tar. The latter are pyrolysis products, released in the upper part of the reactor vessel. These are removed by a spray quench and condensers. The gas then passes through filtration steps, before entering the catalytic synthesis reactors. If a high-FSI bituminous coal were used, there might be a caking problem in the upper bed.



Coal gasification involves dismantling the molecular structure of coal and reassembling the resultant hydrogen and carbon as methane.

The heart of the synfuels plant is

This simple flow sheet shows the original purpose of the Dakota Gasification Plant, which was to make SNG (Synthetic Natural Gas), because of a belief, back in the 1970s, in an impending crisis due to depletion of natural gas reserves. (Since then, the methanation step has been generally modified to produce a variety of other chemical products. Below is a sketch of the arrangement of the 14 Lurgi gasifiers, of the specification shown above.

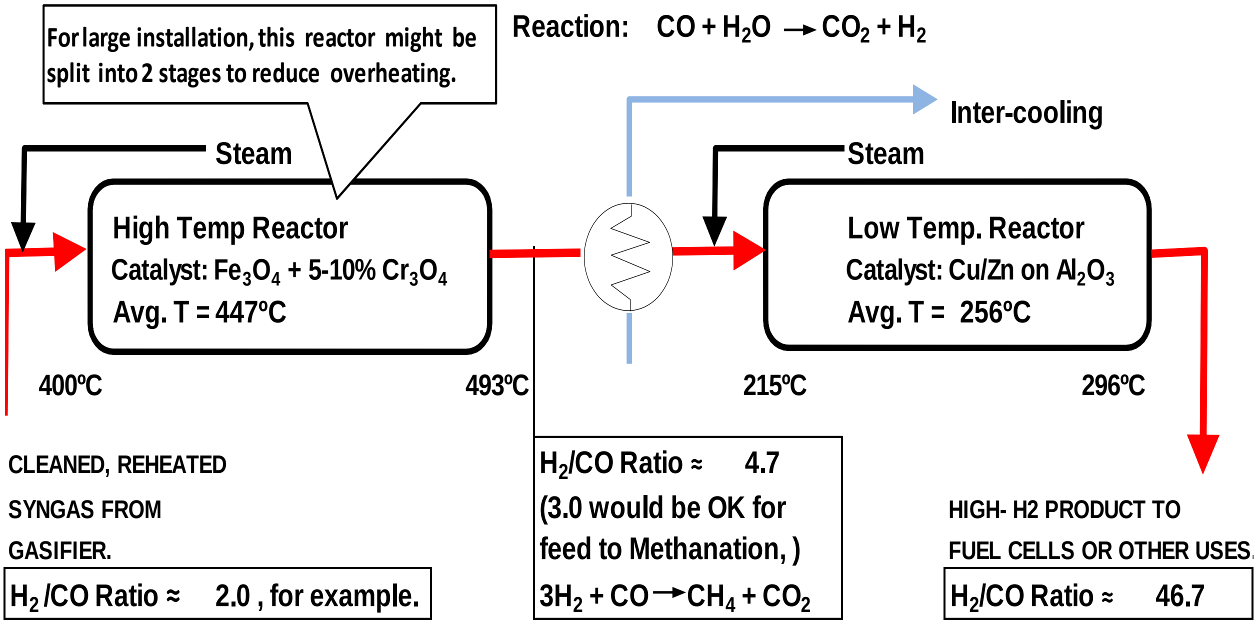


Below is a view of the plant.

Ref.: http://www.rmcmi.org/docs/default-source/default-document-library/mike-just--thriving-in-uncertain-times.pdf?sfvrsn=0,

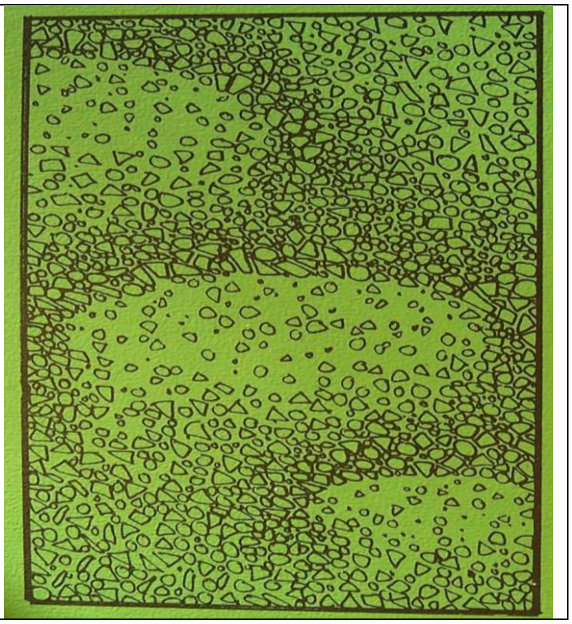
And:,https://netl.doe.gov/File%20Library/Research/Coal/energy%20systems/gasification/gasifipedia/GTC01010.pdf

Following gas cleaning, the next step in any process is adjustment of the H_2/CO ratio to whatever is required for synthesis steps. This utilizes the water-gas shift reaction. The example below shows a relatively complex, 2-stage process step to achieve maximum H_2/CO, such as might be desired for some synthesis reactions or for use in a fuel cell. For methane synthesis, an H_2/CO as low as 3.0 might be acceptable.



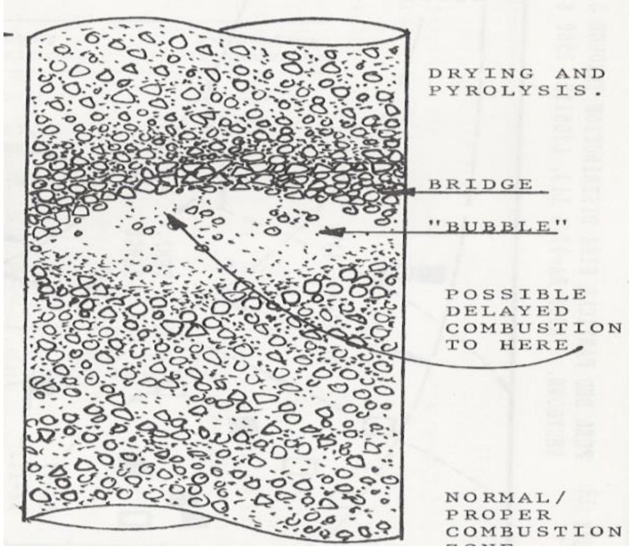
Design trade-off:

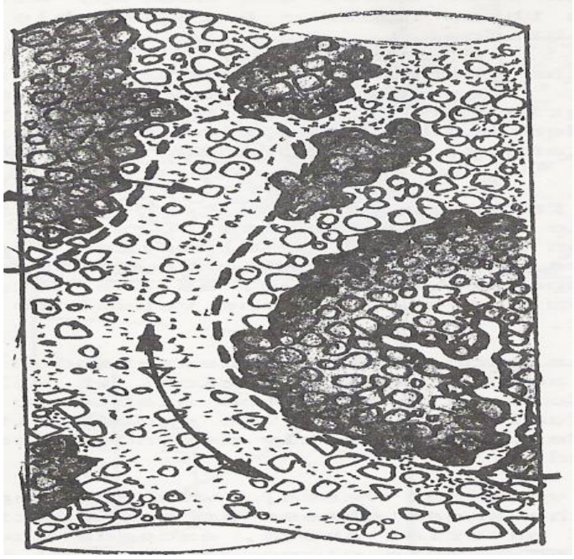
- Select /design gasifier to give desired H_2/CO ratio, if possible, or—
- Select gasifier for efficiency & economy then add a shift converter

In a "fixed bed" gasifier design, the solid as fed is within some fairly narrow range of particle size, is assumed to be of uniform permeability, and the minimum particle size has a terminal settling velocity well above maximum up-flowing gases in the vessel. If, however, the gas flow is increased too high, such as to increase solid throughput – or if the permeability is reduced by excessive fine particles, the bed will start to lift, and temporary bridges will form and collapse. This is now a transitional condition between a fixed and fluidized bed. For a small diameter gasifier, relative to the maximum particle size, this kind of problem becomes more probable. For less-free-flowing feeds, such as chipped wood or recycled tires, and even more extremely, for shredded crop waste or sawdust, this type of problem becomes the dominant design factor	

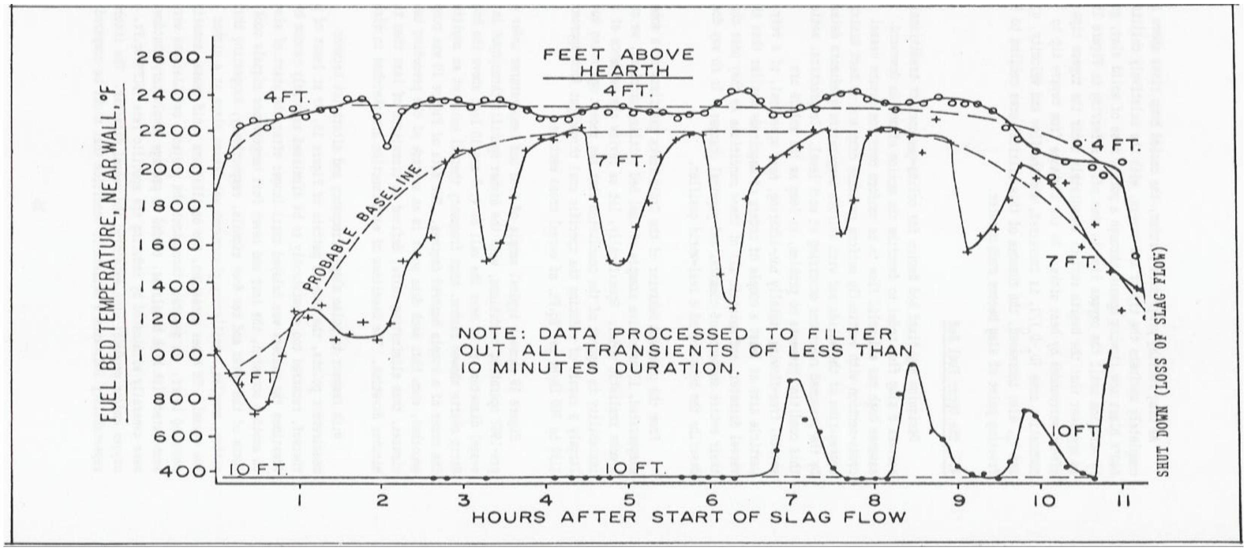
A small, pilot gasifier was used to simulate performance of the above Lurgi Mark IV gasifiers, using the same coals. This unit was found rather than designed exactly for the purpose. It had an active reactor volume of 24" by 20 ft tall. It was a slagging gasifier, with a very hot (2000ºF+) combustion zone at the hearth, so ash flowed out as a molten slag. But the gasification, pyrolysis and drying layers maintained the same temperature, pressure and chemical conditions as the full-sized Lurgi units, producing the same products. (For mechanical operation, this pilot gasifier could be designated as a WCDU - Worst Case Demonstration Unit.) Some of the operating problems created are shown below.

Because of the too-low ratio of diameter to maximum particle size, and high friability of the feed, upper parts of the bed became plugged by dust, allowing temporary bridges to form, thus starving the combustion zone below, which then shifted upward. In other instances, "blow-thru" channels were formed, allowing the combustion zone to surge upward, bypassing part of the bed.





Below is a plot of wall temperatures during a short operating run, at 4ft, u7ft and 10ft above the hearth plate. Note that by 3 hours into the run, the combustion front shifted from below 4ft to a burning bridge area at 7 ft above the hearth. The bridge kept collapsing and reforming at roughly 1.5 hour intervals. Finally, after 7 hours, hot surges at the 10ft level indicated partial combustion channels were reaching even higher, posing a danger of explosive burn-thru to the product gas.

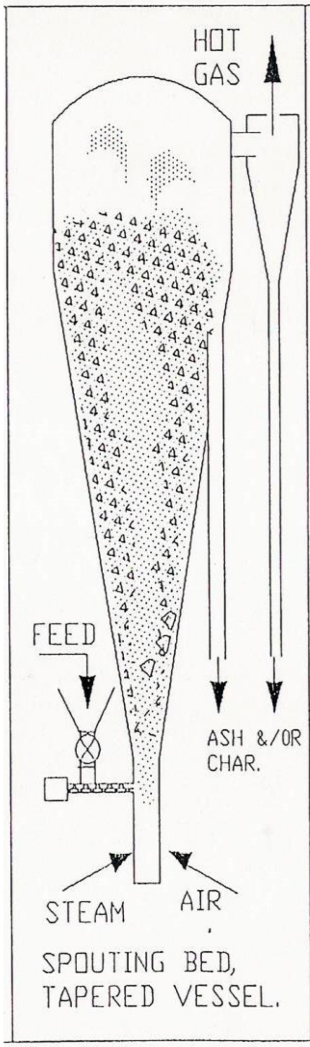


Ref..: “Conclusions of Slagging, Fixed-Bed Gasification of Lignite.” By W.B. Hauserman. University of North Dakota Energy Research Center,

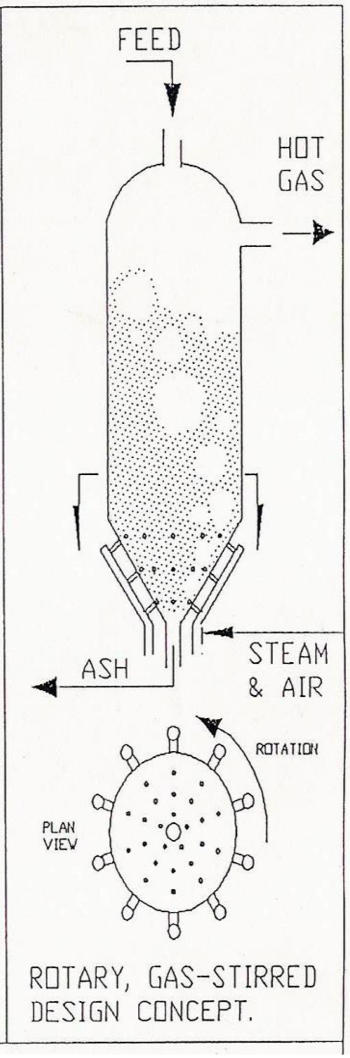
In a properly designed, production scale, fixed bed gasifier, the above type of problem is unlikely to occur. If at all, it is most probable for feed materials with strong agglomeration tendency (bituminous coals) or widely different particle size or composition (garbage). So what design features might be considered to avoid bridging problems? Mechanical stirrers are obvious suggestions, but involve moving parts in reaction zones at temperatures dangerous to the softening points of metals. (The WCDU stared out with a stirrer. It melted.) Some possibilities might be spouting bed or gas-stirred reactor designs, as sketched below.

In the spouting, tapered bed design, the air-steam, upward flow at the bottom is fast enough for complete fluidization. Higher up, it becomes a packed be with a random blow-through channel carrying up all ash or fine residual char to an overflow chute. If the air/feed ratio is high, complete combustion and gasification should occur. For a minimal air/feed ratio, carbon consumption will be minimum, and it becomes a pyrolysis. Any large lumps formed by agglomeration will be kicked back upward and recirculated until consumed. Developmental status: Unknown.

In the rotary, gas-stirred design, the steam/air/oxygen feed is inserted as a high velocity stream, in slowly rotating positions around the bottom. This results in a temporary blow-through channel, moving around the otherwise fixed bed, kicking upward any lumps formed. Developmental status: Cold simulation with sawdust, normally massively bridging and non-fluidizable. With optimum rotation speed, bed was maintained completely uniform and semi-fluidized.



SPOUTING BED, TAPERED VESSEL.



ROTARY, GAS-STIRRED DESIGN CONCEPT.

Fixed Bed Gasifiers - Summary of Design Concerns.

- Bed must have uniform permeability to up-flowing gases.
- Bed settling rate determined by steam/air/oxygen flow, which controls consumption rate of solid feed.
- Maximum pressure drop must stay safely below the bed weight, to avoid lifting fluidization or flow-through.

- For usual “dry bottom” or dry ash designs, maximum temperature must stay safely below the ash fusion temperature, for any feed material.

- Feed properties of concern are any that could cause agglomeration or otherwise loss of “free-flowingness.” These would include the FSI of coals or Angle of Repose for fibrous biomasses.

- Bed material consists only of the solid feed and its residual ash.

- Use of pure oxygen with steam provides higher possible temperatures and much smaller equipment volumes for desired production rate, by elimination of nitrogen dilution. As a trade-off, an oxygen plant becomes the major component of overall plant cost.

- Product gas is normally used for synthesis of methane or higher hydrocarbons, the desired H_2/CO ratio can be partially achieved by adjusting the steam/oxygen ratio. Final adjustment usually requires a downstream water-gas shift reaction.

- Air would be used only if the gas is to b consumed as a direct fuel, at near atmospheric pressure, where a high nitrogen “ride-along” concentration could be acceptable.

The above example (Great Plains Gasification Plant) was just one example of the uses for gasification. Use of syngas to make SNG is not a big demand and probably never will be. But synthesis of motor fuels – gasoline and diesel – may well become a major industry as world petroleum supplies are depleted. This will demand coal and/or biomass feedstocks. Coal is the optimum feedstock, because of it availability in large amounts at single sources, allowing the economy of scale for these expensive, complicated plants. Future design ingenuity is urgently needed to develop smaller scale plants to handle the greater diversity of biomass feeds.

With few exceptions gasifiers alone convert coal or biomass into essential but relatively low-value products: Process heat and electric power.

A few produce syngas for conversion to other products such as synthetic natural gas, purified H_2 or CO as feed to other processes, or other chemicals. (Examples: H_2 for hydrotreating heavy petroleum resins or hydrogenating vegetable oils. High purity CO as raw material for phosgene, the precursor to polycarbonate plastics.) In Section 5, you saw a brief description of the water-gas shift reaction, carried out in separate reactors, following gasification, to adjust the syngas H_2/CO ratio to some specified optimum, required for subsequent reactions.

The biggest potential market for syngas is conversion to vehicle fuels – gasoline, diesel or alcohols – via Fischer-Tropsch synthesis.

South Africa has for years supplied 30~40% of its vehicle fuel consumption from its domestic coal deposits. China is launching major projects, using the same Sasol technology, as a step toward Energy Independence. These use variants of the Lurgi Mark 2 design and possibly fluidized bed designs, such as the eGas shown in Section 5.

In the USA such technology, because it uses coal, is in political disfavor, along with economic demand, because of recent discoveries of new crude oil reserves. Eventually, with realization that now-plentiful reserves of natural gas and petroleum will someday -or some century- be depleted, coal and biomass are the next most realizable source of large scale vehicle fuel production. Thus is the potential importance of the following.

For **Fischer-Tropsch Synthesis**, a stream of purified syngas, of some specified and adjusted H_2/Co ratio, is used to convert the syngas to a huge variety of mostly hydrocarbons, with a broad range of boiling points. This involves a variety of reactions, as shown below. All are exothermic. In large commercially functional designs to date, the catalysts - variable and generally proprietary – are delivered as a slurry, to react with a gas feed at high pressures and temperatures.

Fischer-Tropsch Reactions To convert Syngas to Useful Products

In General: (2n+1)H2 + nCO ↔ CnH(n+2) + nH2O ,

or CO + 2H2 ↔ CH2 + H20

	ΔH, kcal/kmol
Olefins	
$nCO + 2nH_2 \leftrightarrow C_nH_{2n} + nH_2O$	-39,400
Paraffins	
$nCO + (2n+1)\ H_2 \leftrightarrow C_nH_{(2n+1)} + nH_2O$	-39,400
Alcohols	
$nCO + 2n\ H_2 \leftrightarrow C_nH_{(2n+1)}OH + (n-1)H_2O$	-39,400
Methanation	
$CO + 3H_2 \leftrightarrow CH_4 + H_20$	-49,500
Water-Gas Shift	
$CO + H_2O \leftrightarrow CO_2 + H_2$	-9,500

Typical Conditions: 400~600ºF (200~300ºC) 15~40 Atm (200~400 psia)

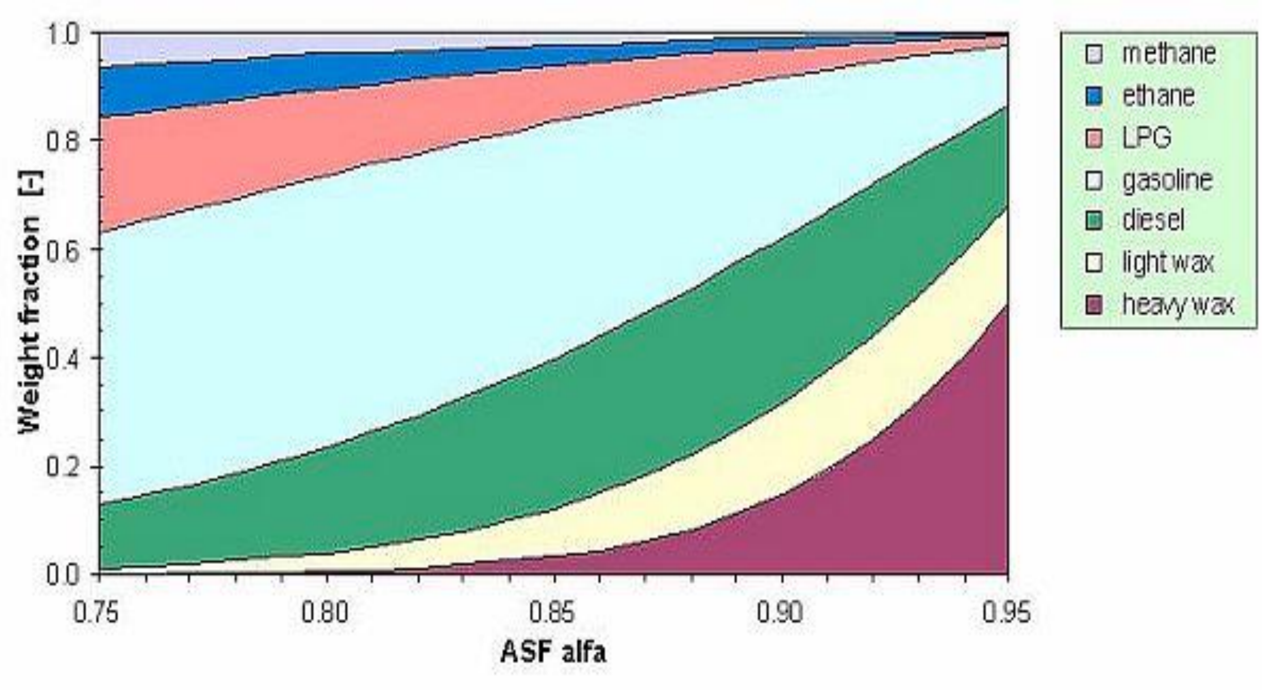
Reaction Efficiencies for Fischer-Tropsch Products

CV = Calorific Value, Btu/Lb-mol "CGE" = $CV_{Products}./CV_{Reactants}$

n	Product	SCV, Reactants	SCV, Product	CGE
1	Methane, CH_4	271,000	212,000	78%
2	Ethanol, C_2H_5OH	407,000	249,000	61%
3	Propane, C_4H_{10}	882,000	685,000	78%
4	Naptha, C_5	1,085,000	837,000	77%
11	Naptha, C_{11}	2,307,000		
8	Typical Gasoline	1,696,000	1,306,000	77%
12	Diesel, C_{12}	2,510,000		
19	Diesel, C_{19}	3,935,000		
16	Typical Diesel	3,222,000	2,368,000	73%

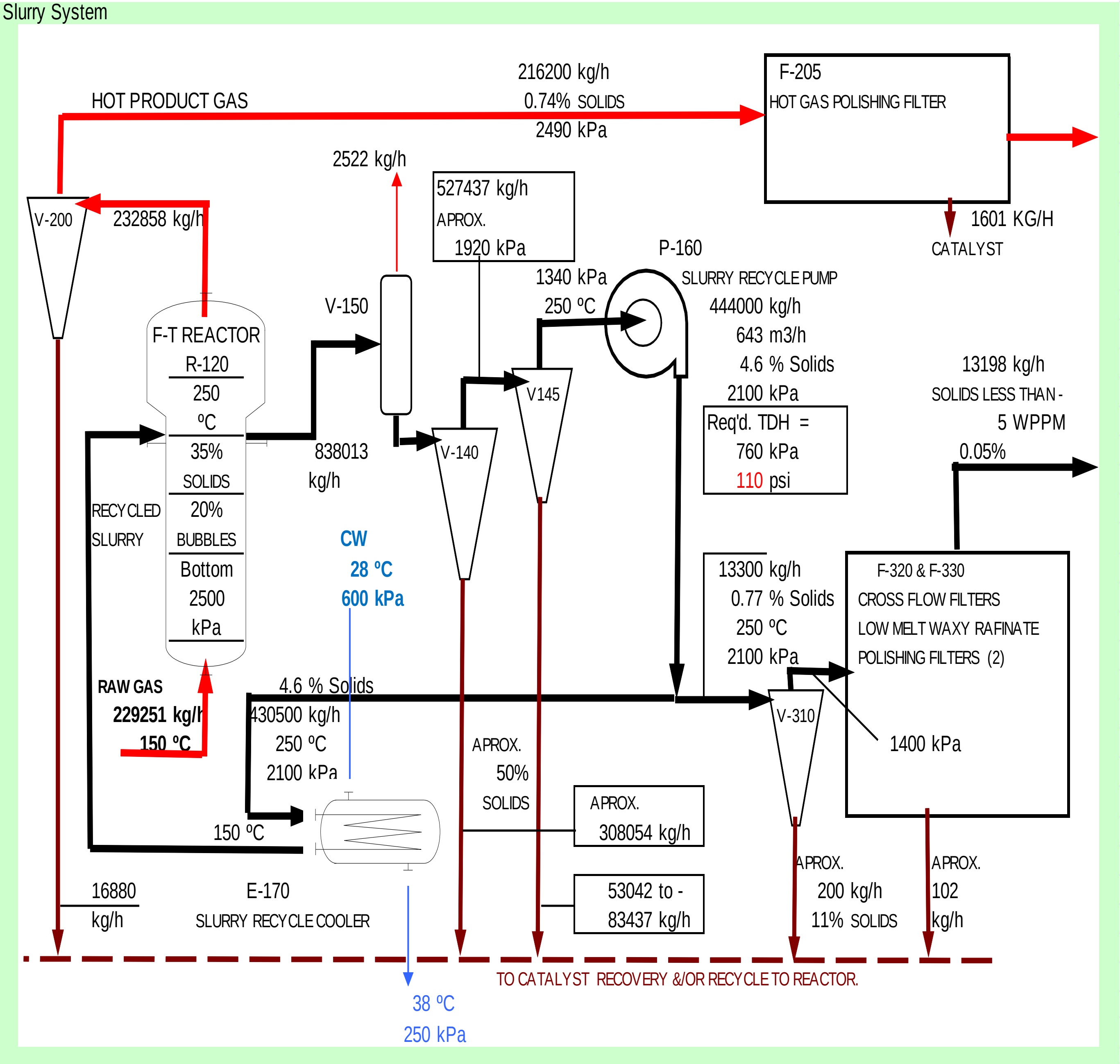
Average (Theoretical Maximum for F-T Conversion) = 74%

Theoretical prediction of the product mix, for a given Feed H_2/CO ratio, catalyst, T & P, is nearly impossible, and so is determined by laboratory tests. An empirical model has been proposed, in which product distributions are roughly predicted from an "ASF a" factor, which is complex formula combining phase equilibria of all components and process conditions. While beyond the scope of this work, the following illustration shows the range of products that can be produced.



The raw F-T product mix is roughly as broad as crude petroleum. So to separate this “dog’s dinner” of useful components, requires a process sequence that can approach the complexity of an oil refinery. And will not be dealt with here’

To operate an F-T reactor, requires massive heat removal, plus continuous extraction and reactivation of the catalyst. The following excerpt from a preliminary design flow sheet shows a reactor plus the catalyst recirculation system for a typical scale F-T synthesis plant. (Design of such a system, plus downstream separations, presents challenges to all the core components of a chemical engineering curriculum, and especially to slutty handling.)



2500 kPa = 362 psig Syngas H_2/CO ratio unknown.

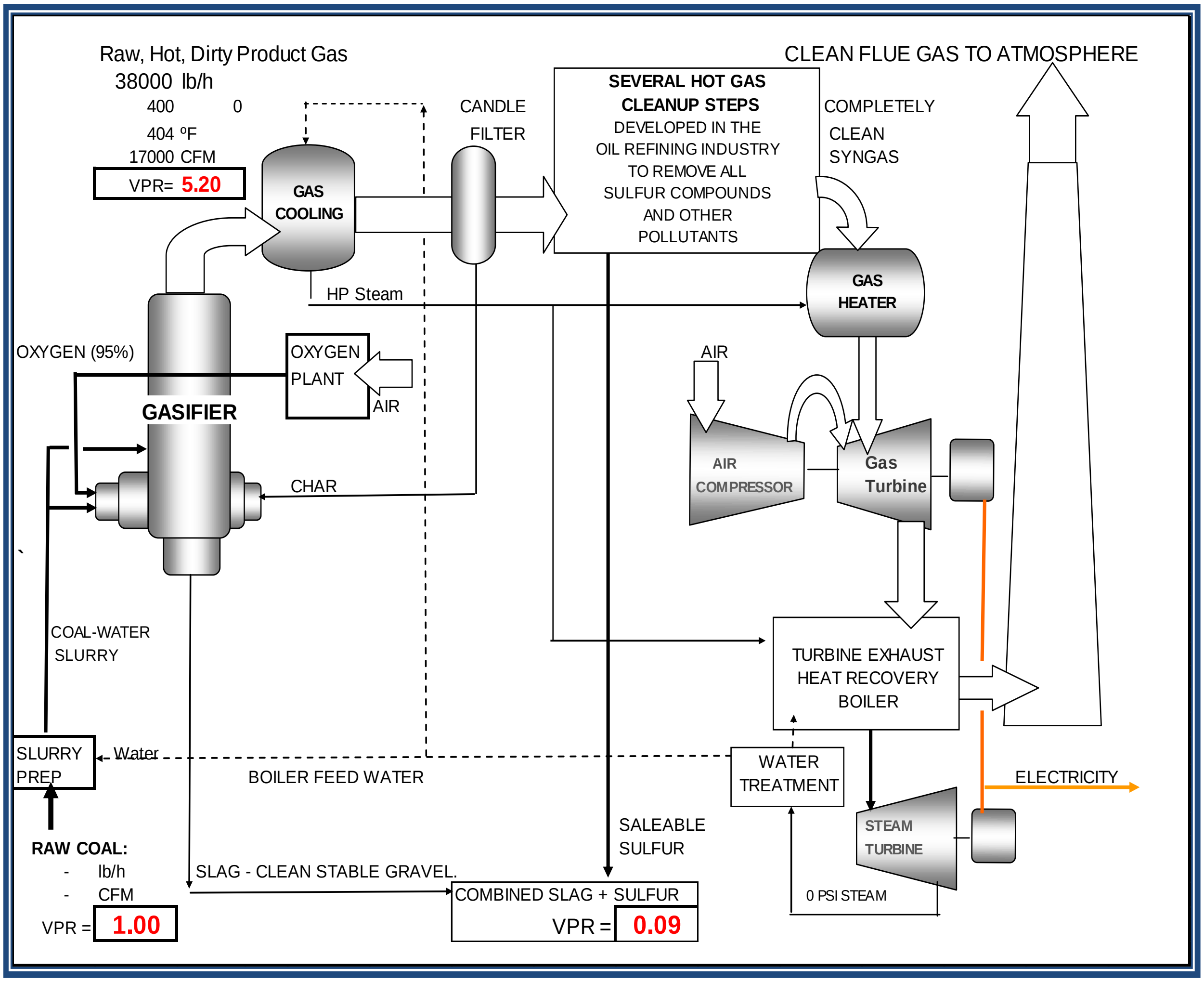
F-T plants to date are quite large, needed to take full advantage of economy of scale. The monster shown below is probably quite similar to the hypothetical unit in the flowsheet above. Typically, it has 3 sets of internal cooling coils, making steam, to remove the exothermic heat of reaction.

6. Pressurized Gasification with Steam and Pure Oxygen for Large-Scale Power Generation

Definition: IGCC = “Integrated Gasifier with Combined Cycle”
Objective: Produce clean high-Btu gas for use in most efficient electric power generation.

Relatively simple gasification on large scale to supply syngas to conventional gas turbine(s) with turbine exhaust supplying heat to conventional steam cycle getting double use from heat.

This example will consider a high temperature, entrained flow reactor with ash leaving as a molten slag. “Entrained flow” is the upper limit of a fluidized bed, where the reacting volume is not completely mixed, but is flowing consistently upward. Very finely ground coal is fed as a slurry, with carrier water providing the required steam.

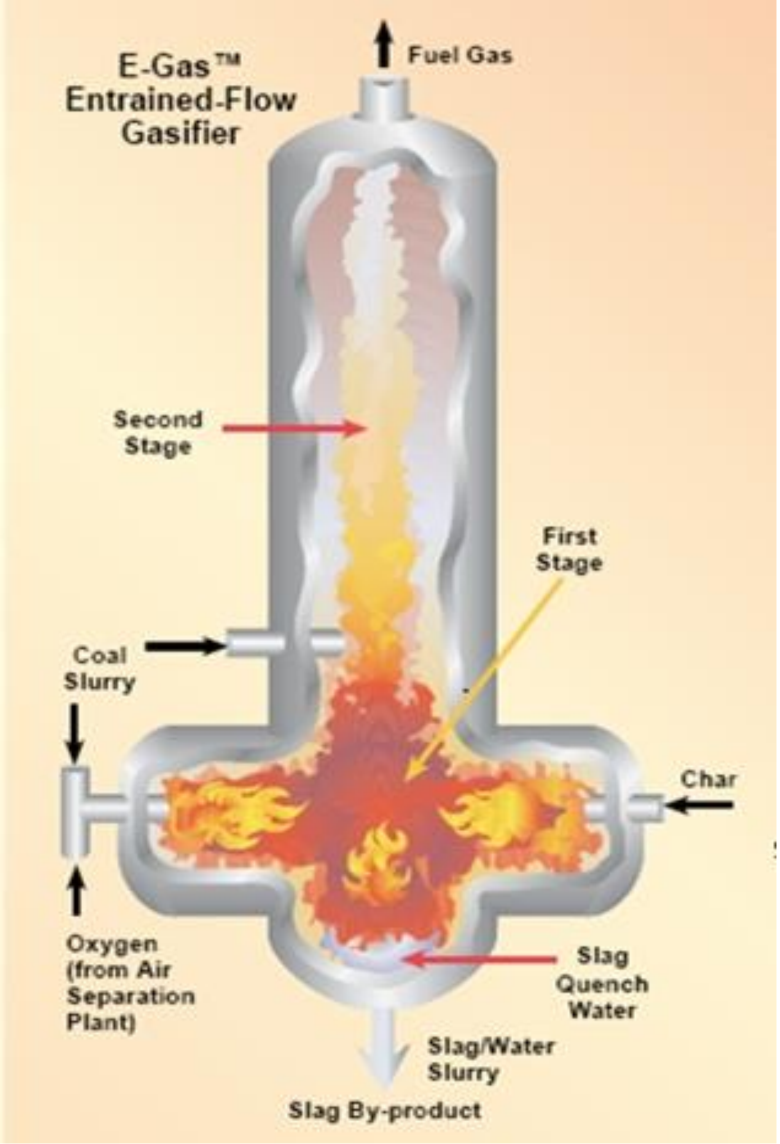


Proposed Mesaba Project Northern Minnesota.

Ref.: www.excelsiorenergy.com
And: “The Impending Renaissance of Coal Gasification in the Upper Midwest” by William B. Hauserman, PE and Robert S. Evans. (AIChE Upper Midwest Annual Symposium, 4/11/2006)

“VPR” = Volumetric Pollutant Ratio = The relative volume occupied by all pollutants (Sulfur and ash, in coal) at different points throughout the process. For coal in ground, VPR =1.

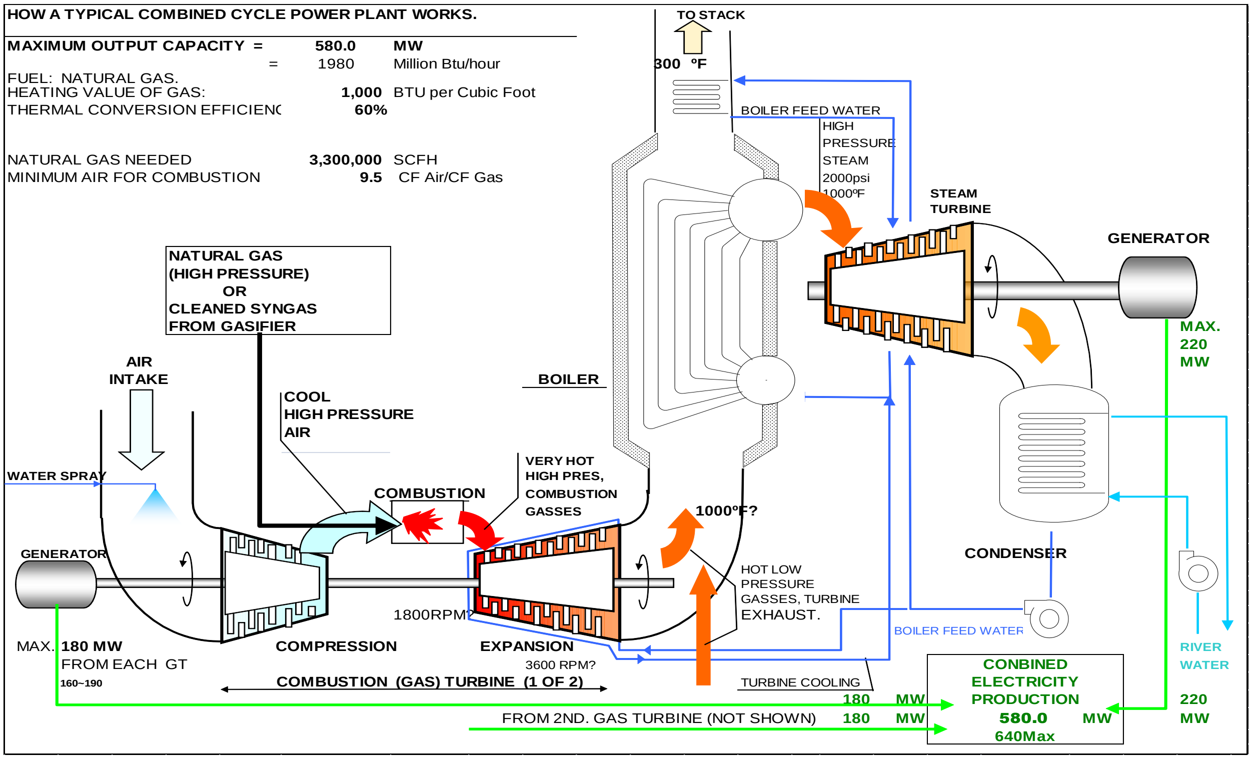
Selected Design: High Temperature Entrained Flow Gasifier, “**eGas**”



- Entrained flow, slagging gasifier
- Co-current flow: coal, agent and gas flow upwards, 2 stage feeding
- Wet feed, coal slurry
- Very fine coal: < 150 µm
- Caking or non-caking coal
- Unlimited tolerance to fines
- Short residence time (seconds)
- Ash content: pref. <25%
- Ash: melted and removed as slag
- Ash melting temperature <1200ºC
- Operated in Holland, Spain, China

Ref.:
https://www.cbi.com/getattachment/174013d4-ab9d-4b53-8e6a-cc1b3a88d46c/E-Gas-Gasification-Technology.aspx
And:
http://www.mcilvainecompany.com/Decision_Tree/subscriber/CO2DescriptionTextLinks/ConocoPhillipsPhilAmickJune05.pdf

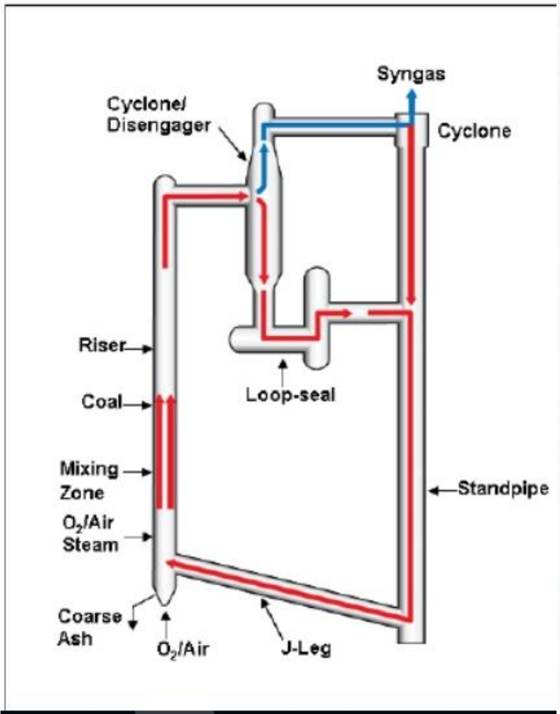
For further definition, a sketch of a typical IGCC plant is shown below. Specific numbers are for a relatively new installation, by Northern States Power, in St. Paul, MN, burning natural gas, providing peak power, with base-load power provided mostly by coal and nuclear plants. I can be put on line within a couple of hours from a cold start, and respond to load requirements within minutes, compared with several days required to start up a coal-fired plant.



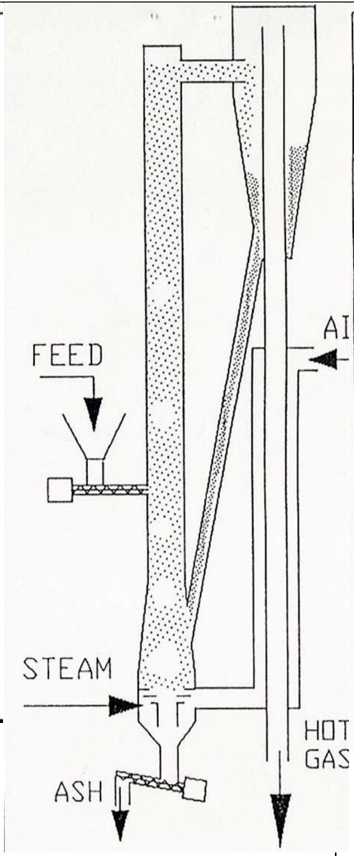
This combined process is well demonstrated in commercial operation in some locations, with further development of multiple options still under development by USDOE.

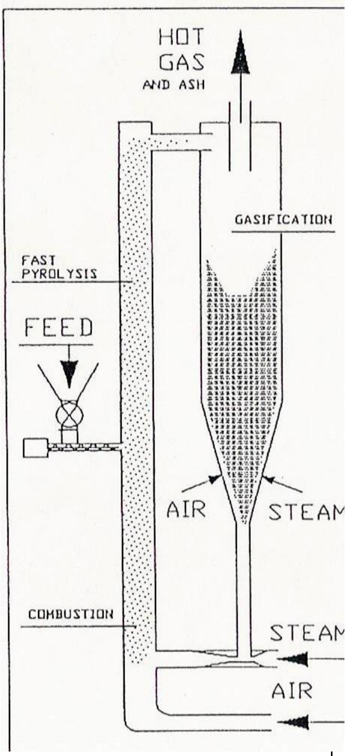
WABASH RIVER IGCC DEMONSTRATION PLANT
Ref. https://www.netl.doe.gov/research/Coal/energysystems/gasification/gasifipedia/wabash

As to the gasifier itself, it is a “transport” or “circulating fluid bed” or “entrained flow” design. Below are schematics of this category, all designed for free-flowing solids, with relatively low temperatures (below feed’s ash fusion temperatures). The eGas design, however, is a high-temperature slagging design. All of these have in common that feed is quite fine and all reactions occur within a short time, as the feed is carried upward in a hot riser section, and then separated, with remaining ash separated and recirculated to the bottom. In eGas, because the hot gas must be used at full pressure (at least 150 psig) for use in the gas turbine, the gas is cooled before un-reacted char is separated (by costly ceramic candle filters) for recycling.



KBR Gasifier. Ref: https://www.scribd.com/document/96530066/KBR-s-Transport-Gasifier-TRIG-An-Advanced-Gasification-Technology-for-SNG-Production-from-Low-Rank-Coals





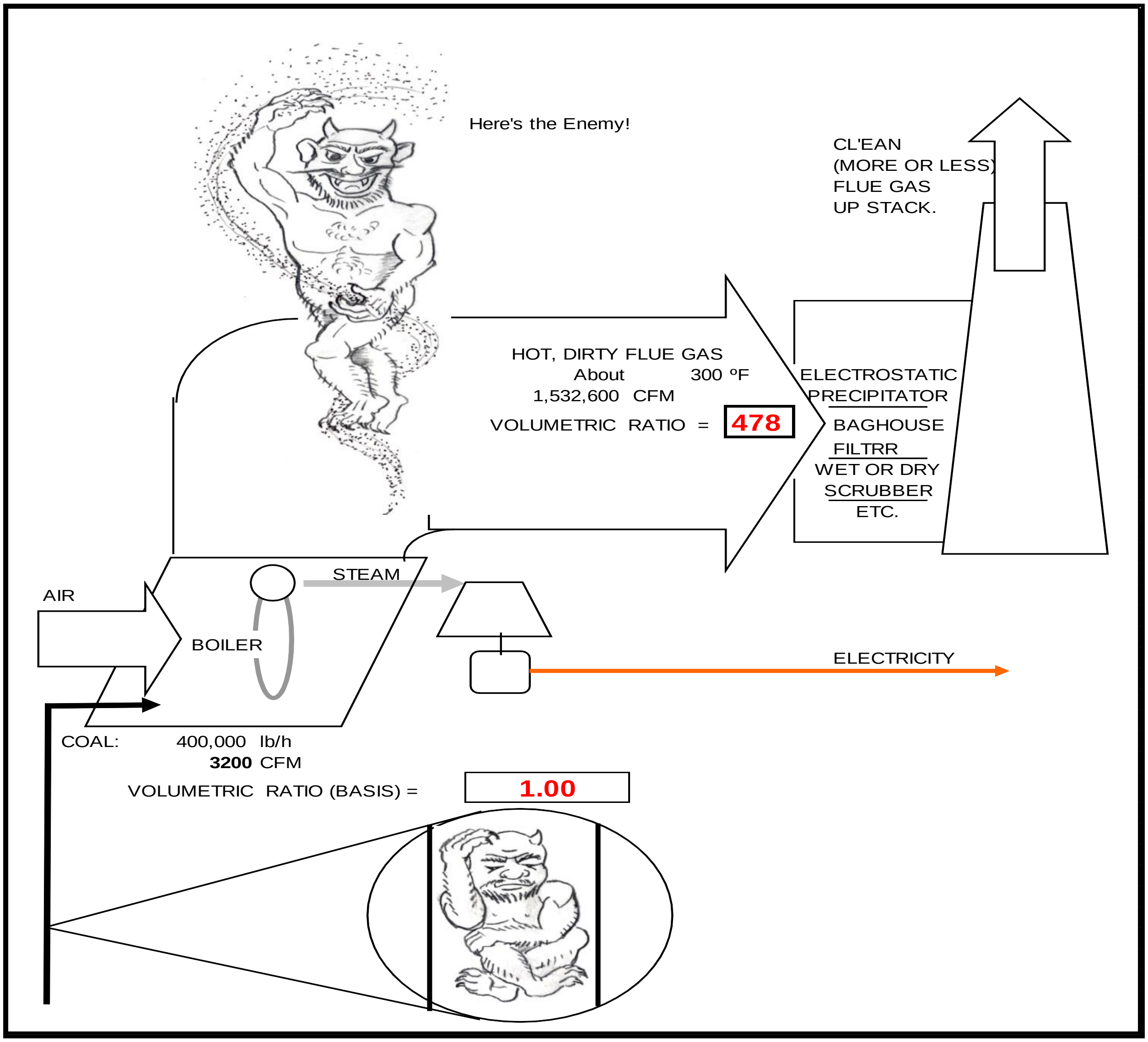
In these designs, all pyrolysis products (condensable liquids) are vaporized during the short residence time in the up-flowing entrained bed. It will then be condensed/recovered in subsequent spray wash and condensation steps. All residual carbon is recycled, as many times around as necessary, for complete gasification (steam-char reaction). If there is a demand for a residual carbon product, the char recycle leg can be diverted and cooled, as product, converting the system to a pyrolysis process. In such a case, some or all of the product gas will need to be recycled to the combustion zone as fuel for process heat.

ENVIRONMENTAL RATIONALE FOR BIG EXPENSIVE IGCC PLANTS

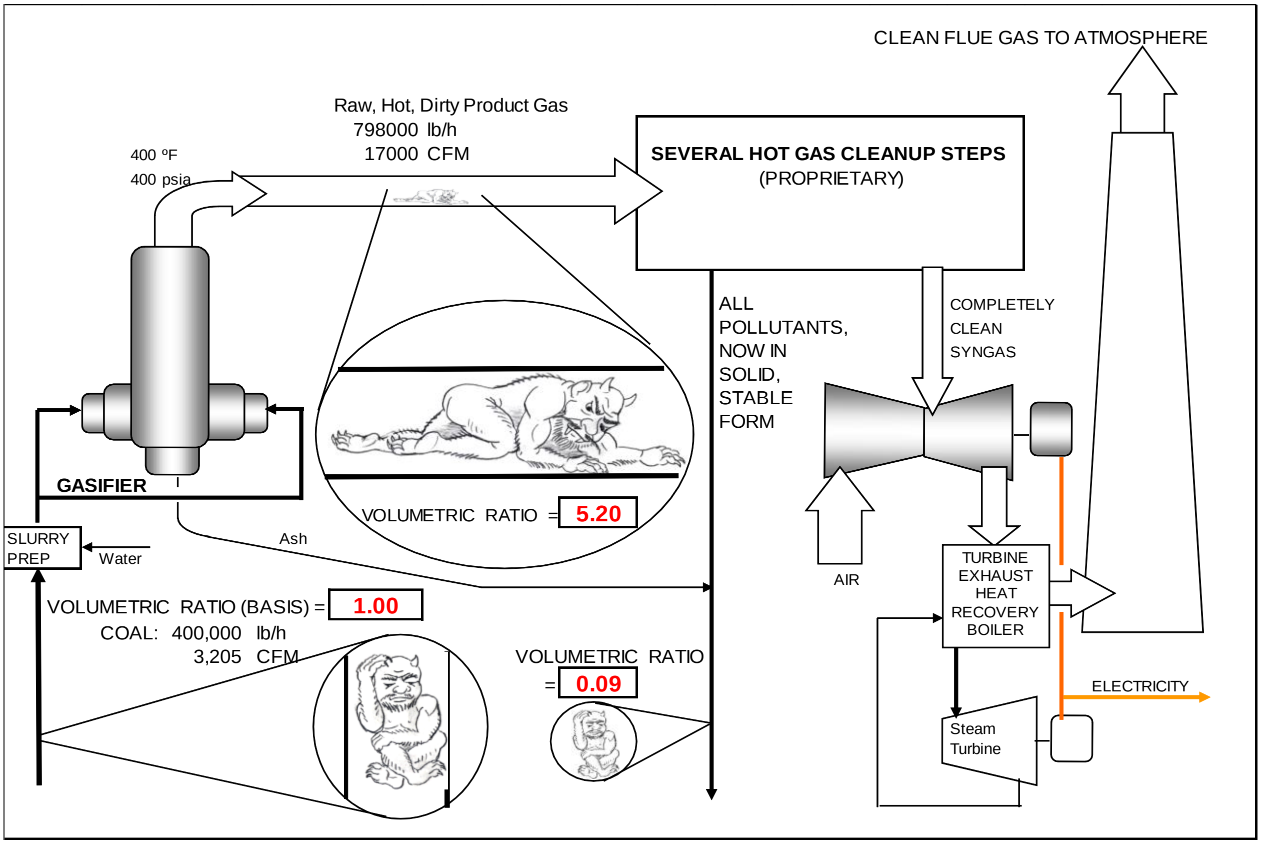
EFFICIENCY: In spite of added cost of O_2 plant and compression power, Combined Cycle efficiency (using heat twice) may reach overall conversion efficiencies of around 45% compared with as low as 30% for the older conventional coal-fired power plants in operation.

CO_2 EMISSION per kW-hour of power is reduced in direct proportion to increased efficiency.

POLLUTANTS (Ash and Sulfur) in coal are like a malignant troll or *djinn* locked into each unit volume of coal (see below). When burned in a traditional power plant, He escapes – expanded by maybe 500 times, joyfully spreading pollution! -Unless recaptured by big, expensive flue gas scrubbers or Electrostatic Precipitators. How do we put the *djinn* back into a bottle for disposal?

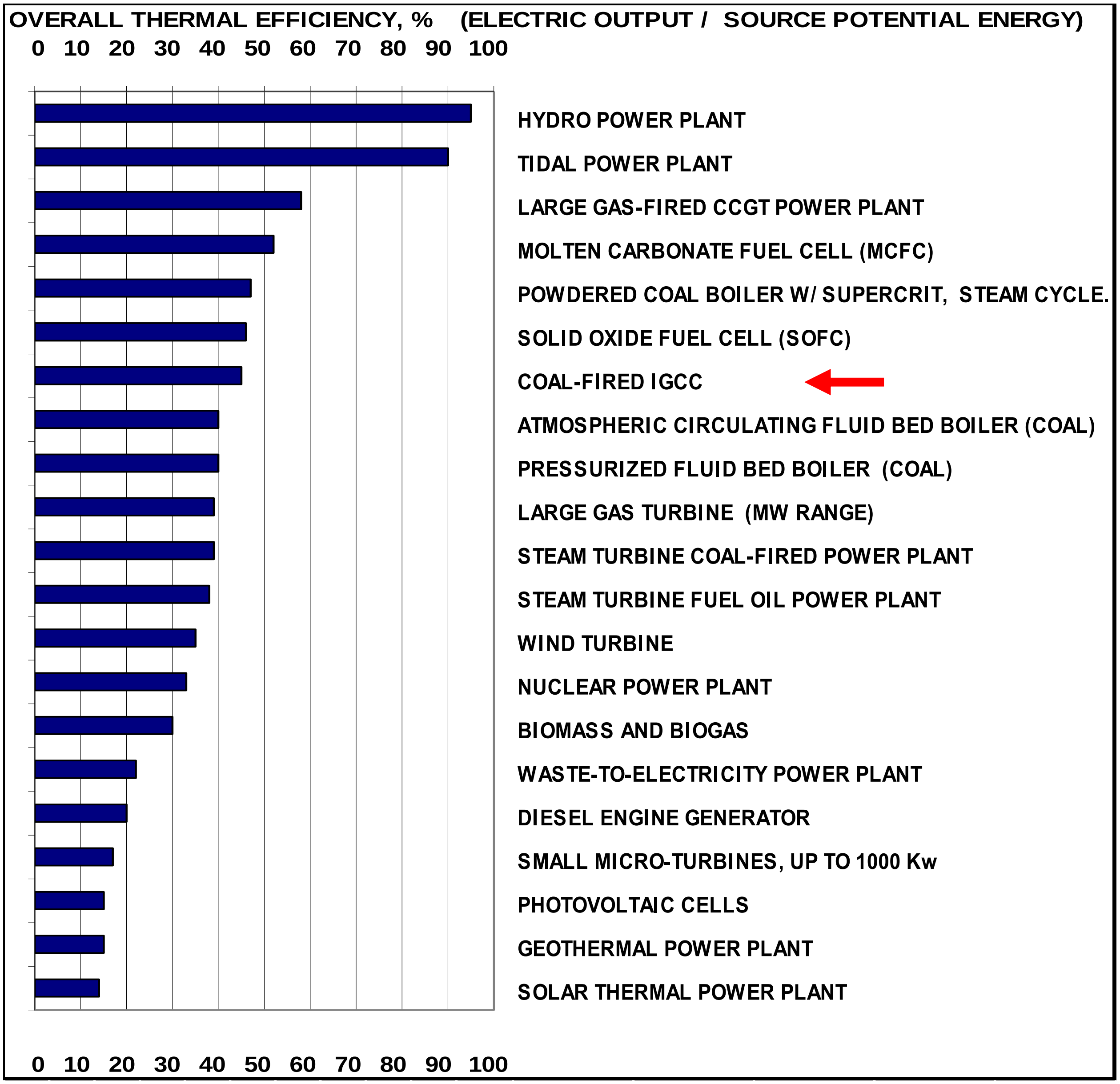


Instead of simply burning the coal, it can be used in a high-pressure (400 psi) IGCC plant using pure oxygen, as described above. All pollutants are contained in the raw product gas stream for capture and containment. Under these specific conditions, our *djinn* may be awake and quite malignant, in the form of dust and sulfur compounds, but squeezes unto a pipe, at a volumetric ratio of only 6.2 times His original volume in the raw coal. From there the gas stream goes through a complex-looking sequence of gas cleaning and desulfurization steps, beyond the scope of this work, and finally concentrated in compacted blocks of ash and pure sulfur, sold as a byproduct. The ash and sulfur, not diluted thru raw coal, will now occupy a volume of only 9% that of the original as-mined coal. Thus our *djinn* is now compressed and hibernating, harmless for eternity. The process is thus completely non-polluting.



As to efficiency, the chart below shows Overall Thermal Efficiencies of various energy conversion processes. As a refresher to be remembered, OTE is the ratio of energy delivered – in this case as electric power – to the potential energy of the fuel or source, both converted to the same units. The overriding objective of (almost *****) any design project is to maximize this efficiency, to get the most energy, in kwhr (kilowatt-hours) delivered per energy received at source. For any combustible or gasifiable material, OTE is kwhr delivered per 3413 Btu of HHV (Higher Heating Value) received. The factor 3413 = Btu/kwhr equivalent. This then defines the economic criterion of getting the maximum value in electric power from that received, as Btu/hr (ln/hr x Btu/lb) of stuff delivered. This also defines the economic criterion of getting the most electric power per amount of pollutants in the stuff received. **If** CO_2 output avoidance is considered as a criterion, increased OTE is a measure of electric power per CO_2 released.

***** An economic exception to the quest for maximum efficiency, is in processes to consume municipal solid waste, where any disposal facility normally receives “tipping fee” for receiving it, which is a major input to a plant’s overall profitability, measured in $/kwhr of power sold. So a plant of lower OTE gets paid to receive more garbage, and is thus more profitable – but generates more pollutants and CO_2 than a higher efficiency plant.



Note: This graph was developed sometime prior to 2007. Source now lost. Since then the efficiency of photovoltaic power has increased greatly.

Summary – Air or Pure Oxygen

- An oxygen plant (cryogenic air separation) may be the most expensive single capital cost component of a gasification process and requires parasitic power consumption.
- For all "air-blown" gasifiers N_2 will make up half or more of the raw product gas. So all equipment will require twice the volume or more, and corresponding cost.
- For downstream applications requiring higher pressure (gas turbines or synthesis steps) compression of N_2 would require excessive power consumption.
- For most synthesis processes the presence of N_2 is unacceptable.
- The presence of N_2 is essential in ammonia synthesis but can be provided at pressure by the air separation plant.
- For use of product gasses in atmospheric boilers or engine gensets, air-blown gasifiers are generally acceptable.

Summary – Atmospheric or pressurized

High Pressure gasification requires –

- Compression of air* (capital and energy cost).
- More complex, exacting solid handling design.
- More costly (per volume) equipment & piping.

As trade-offs against –

- More compact equipment (gasifiers & downstream).
- Requirement for pressurized applications, like gas turbines and synthesis steps.

(* Steam and O_2 come inherently pressurized)

7. Pyrolysis of Biomass, Rubber and Plastics

Relationship between Gasification and Pyrolysis.

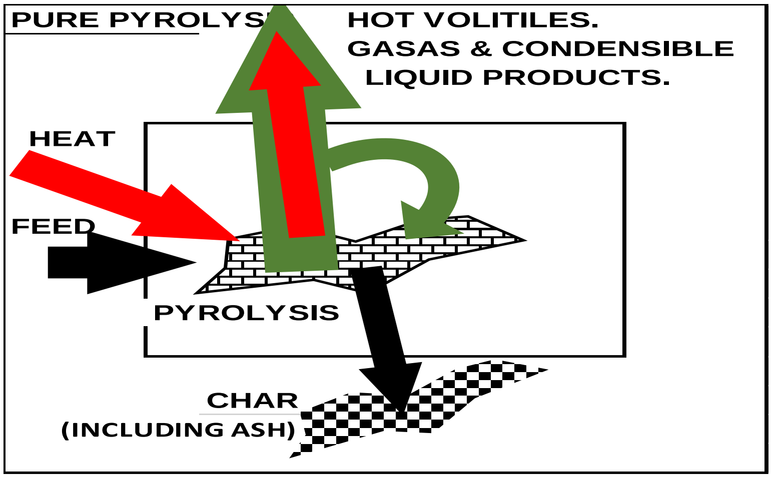
- Both are pathways for thermal conversion of carbonaceous solids to liquid or gaseous products.
- Pyrolysis is the chemical first step in Combustion or Gasification of any carbonaceous material.

The key differences between them.

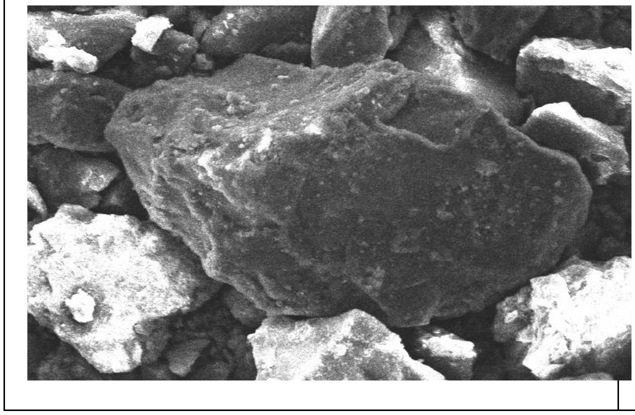
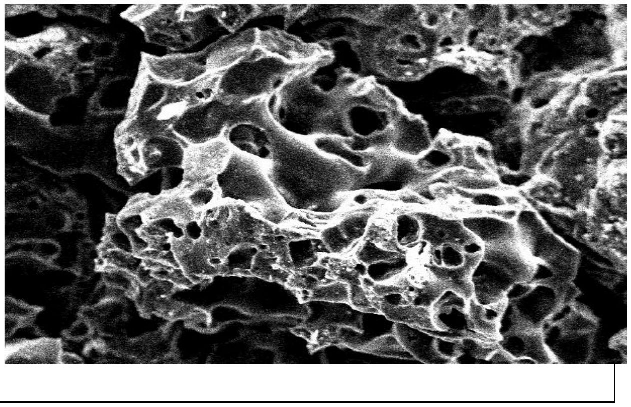
- In all gasification processes heat is supplied by combustion of the solid feed. For pyrolysis alone, heat is supplied from some indirect source or supplemental fuel.
- In all gasification processes, pyrolysis products (VM, Volatile Matter) are a nuisance, causing or contributing to most operational problems, if not consumed immediately as they are formed. For pyrolysis alone, these condensable products are a valued product, to be condensed and recovered.
- In all gasification processes, all residual carbon (FC, Fixed Carbon) is completely consumed by the steam-char reaction, to form the major valued product (H_2 and CO). For pyrolysis alone, the FC is a values coproduct.

In gasification, all reaction heat is usually supplied by immediate, intimate contact between exothermic reactions and receiving endothermic reactions, so no heat transfer surfaces are involved. Heat transfer calculations are thus not needed. For pyrolysis alone, heat may be supplied.

- by direct contact with an externally heated gas stream,
- by direct contact with hot gasses produced by combustion of part of the feed material, or
- by direct transfer from a heated wall to the solid feed, requiring estimation of solid to flowing solid heat transfer.



Intended pyrolysis products are liquid products – at near ambient conditions – and solid char. The char is always of high porosity and lower bulk density than the solid feed. Shown below are some SEM (Scanning Electron Microscope) views of coal particles, magnification somewhere in the 400x to 1000x range, showing pores created by removal of VM by pyrolysis. The high porosity gives this char a high specific surface (cm^2/cm^3) and thus absorptive capacity. If charcoal is the intended use, the high specific surface makes it more easily ignitable and faster burning. For highly absorptive, activated charcoal, the porosity is increased even further by subsequent mild, partial gasification, removing carbon and leaving ever more and smaller pores. Referring to the complex, typical molecular structures sketched in Part 2 of this work, pyrolysis consists of snipping off the less stable, often oxygen-containing branches that rearrange themselves into condensable liquid molecules. Subsequent activation, using the steam-char reaction, digs deeper into the carbonaceous structure, leaving only the most refractory, stable ring structures.

Raw Coal - kind unspecified.	Remaining char, after approx. 30% loss by pyrolysis at 1750ºF
	

Pyrolysis was defined by Reactions 2 and 9, in Section 2 of this work. It is a complex series of reactions, highly variable for different materials, during the disintegration of elaborate, solid molecular structures to light, volatile liquids and non-condensable gases. And these reactions are not even all one-way. Heavy molecules in the vapor state may further pyrolyze to lighter vapors and solid carbon, which can deposit where it's not wanted, like causing agglomeration of fluidized solids. Condensable pyrolysis liquids from coal and synthetic runner are very nearly all hydrocarbons, while those from biomasses are a wider array, of alcohols, organic acids, aldehydes, ketones and other compounds, of lower fuel value and mostly water-soluble. Unlike most gasification processes, the products of pyrolysis vary with the rate of heating and the time at temperature. Following is a table showing approximate distribution of vapor, gas and char products for different pyrolysis rates. It is based mainly on biomass, but also applies to rubber and probably to most plastics.

- If the process objective is to produce liquid "synfuels" product, short residence times at high temperatures are necessary.

- If the desired product is the solid char, such as for charcoal, activated carbon, or metallurgical coke (from bituminous coal). a longer, lower temperature "baking" process is preferable.

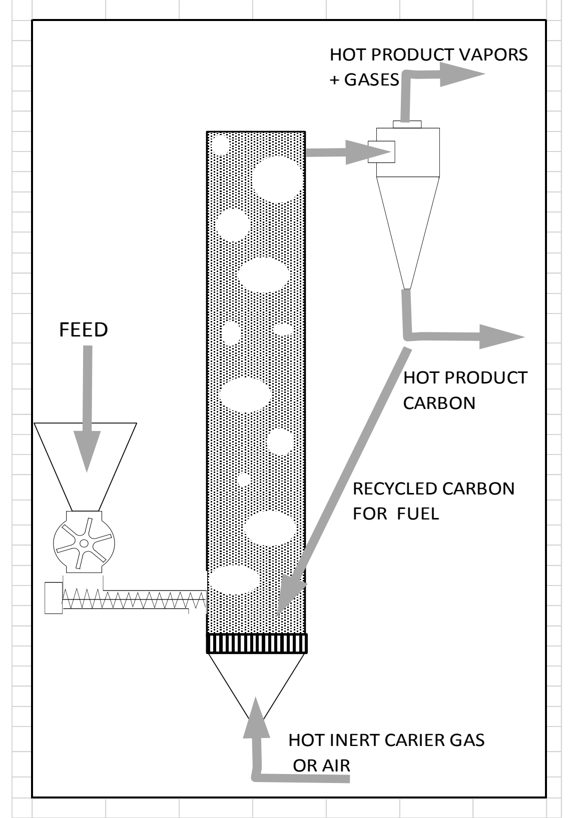
DFINITION OF PYROLYSIS MODES WITH TYPICAL PRODUCT YIELDS. (All numbers approximate.)

Mode	Temperature	Residence Time		Typical Yields		
		Solid	Vapor	Liquid	Char	Gas
Fast	500ºC 930ºF	1 sec	Very short	75%	12%	13%
Intermediate	500ºC 930ºF	Moderate	10~30 sec	50% (1,	25%	25%
Slow	400ºC 750ºF	Very long	Very long	35%	35%	30%
Torrefaction	300ºC 570ºF	Long	Long	Incl. w/ gas	85%	15%

Ref.: "Biomass Pyrolysis," by Tony Bridgewater, Bioenergy Research Group. Aston University, Birmingham B4 7ET, UK. 12 October 2010G. (This reference is recommended for further reading.)

Below is a generalized sketch, showing the core of an entrained flow, fast pyrolysis process, designed primarily for condensable liquid products. Here, a solid feed – generally of some finely ground biomass is fed into the column of rising hot carrier gas. The feed is carried upward for some selected residence time, say 1.0 to maybe 20 seconds, as fast pyrolysis proceeds. It then goes into a cyclone, still at temperature, with reactions still going on, as residual solids are separated. Vapors are then cooled and condensed, probably by a spray quench. The non-condensable gases can be burned externally, to pre-heat carrier gas, and to generate inert carrier gas. There are multiple design possibilities possible. Note the similarity of this design to the entrained or circulating bed gasifiers shown in Section 6, the difference being that for pyrolysis, less heat is required, no steam is injected, and all the carbon is not consumed.

- For maximum yield of condensable vapor products, a hot, oxygen-free carrier gas should be provided, requiring an external heat source.
- If all volatiles are not stripped from the feed within the residence time, residual solids may be recycled, for longer total solid residence times.
- For the process to be energy self-sufficient, some of the char can simply flow back to bottom of the column, to be burned by air, somewhere below the feed entry level, to minimize burning of volatile products.
- The amount of air, or pre-heated inert gas, is determined by the maximum feed particle size and the vessel diameter, to provide the required upward flow to provide a specified residence time.
- For air-to-carbon ratio is limited by the amount of carbon to be burned, to avoid burning of valuable volatile products.



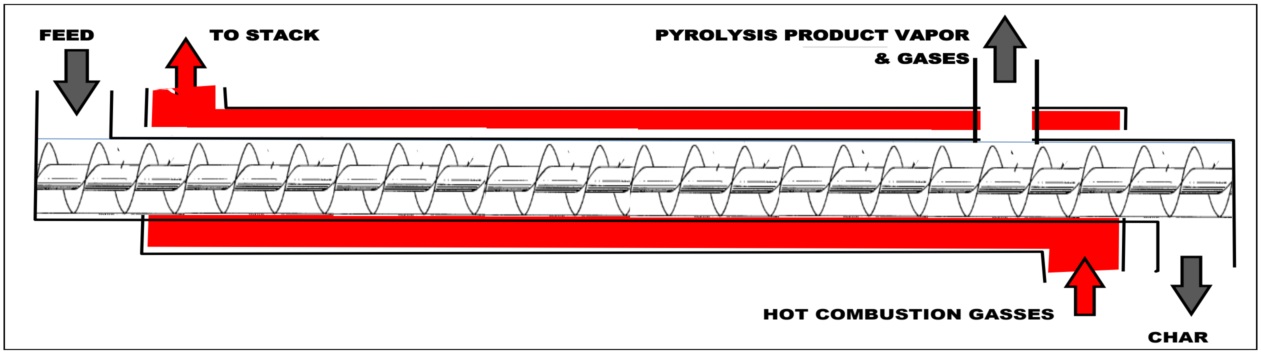
If the upward flow of gasses is slower, and the diameter greater, and/or the feed coarser, this design will be a fluidized bed, rather than entrained. Then it becomes an intermediate to slow pyrolysis process, producing less liquid and more char. With longer residence times, and depending on the feed, the possibility of agglomeration increases. A variation on this design could then be a circulating fluidized bed of hot sand, to provide more mechanical and thermal uniformity.

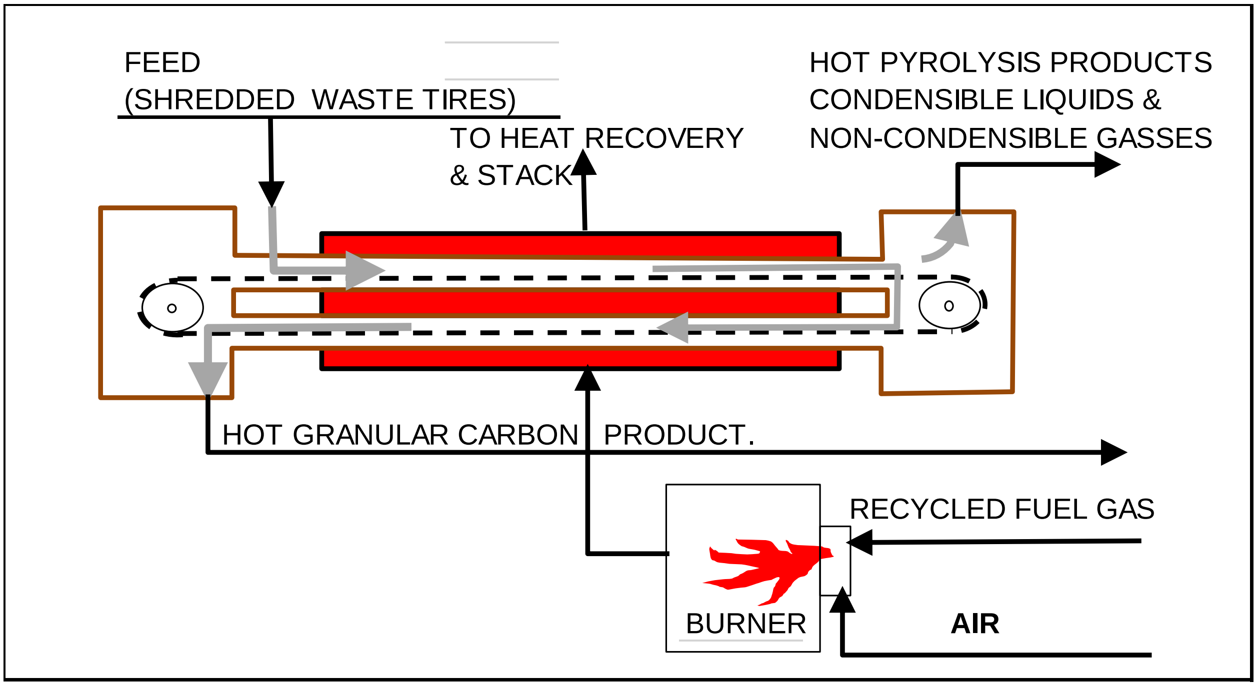
For very slow pyrolysis of biomasses with long solid-vapor contact times, reverse pyrolysis (Reaction 9) occurs, recombining fragile residual char into more durable agglomerations. This is what happens during charcoal production. This is defined as torrification, in the table above. This is also the basis of charcoal production – the oldest and simplest pyrolysis process, where wood is simply partially, burned, very slowly, by batches, in a simple enclosure with limited air access.

Since wood charcoal is fragile, batch processes are essential if the product is sold in “natural” lump form, as used in most developing countries. Where the raw charcoal is produced in fine, crumbled, granular form, as from a continuous process (See below) briquetting is necessary. At least one major US produce of bar-b-cue briquettes has produced them from lignite, which is quite acceptable for cooking if the sulfur content is very low and pyrolysis id near-complete, to eliminate volatiles that would be un-appetizing for grilling use. This requires use of binders that must also be culinarily acceptable. One design for production in Haiti, using a local lignite, used lignite char, pyrolized at 1400ºF, with 15.3% bagasse (sugar cane waste) and 6.1% molases and 3.1% $Ca(OH)_2$, as a binder. Ignitability of briquettes is an essential property. For this, the Haitian design used 2.0% $NaNO_3$.

As to heats of reaction, for a credible process energy balance, those of all the reactions in gasification (Reactions 2 through 8), following pyrolysis, are known, as handbook data. But the heat of pyrolysis, being composed of multiple sequential and sometimes reverse reactions, are highly variable, depending on the rate of reaction. Se fast and slow pyrolysis. In gasification processes, the initial pyrolysis is quite fast, and the endothermic required to sustain it is almost insignificant.

For materials that go through a sticky, soft or semi liquid phase before pyrolysis gets started, such as rubber and plastics, agglomeration cannot be avoided, and is best dealt with by mechanical stirrers. Most common designs are some form rotary kiln, used in batch processing. For continuous processes, screw or drag-chain reactors, with external heat sources offer closer continuous control. Independently of other variables, the solid residence time is manually set by the speed of the screw or conveyor chain drive.





Ref.: ecocarboninovations.com

In both of these designs, feed is heated by direct contact with a vessel wall, from which an otherwise sticky mass is continually scraped and re-mixed. The mechanical challenges of these designs are

- To provide for flexibility during differential thermal expansion of vessels and moving parts.
- To maximize turnover of solid material in contact with the vessel wall.
- To maximize heat transfer by scraping any agglomerations off the vessel wall.
- To minimize wear by avoiding tight contact between moving parts and vessel walls.

These last two challenges are trade-offs – of one at the expense of the other.

As a specific example, consider the drag-chain design, in a process to pyrolyze waste tires, for recovery of diesel-like hydrocarbons, high quality char, for eventual conversion to activated carbon, and reclaimed steel wire, with enough non-condensable fuel gas to provide process heat. In this process, most of the steel wire in tires was ripped out prior to shredding tires to approximately 1 cm chips for feeding. The solid carbon product (38.4% of feed) contained a small amount of ash and small fragments of wire. Along with it came un-pyrolyzed rubber fragments, amounting to 4.4% of the feed, to be separated and recycled to the feed.

For gasification, pressure is determined by the requirements of downstream applications (synthesis or gas turbines). This pyrolysis process, for contrast, is operated under vacuum conditions, to promote vaporization of volatile liquid products as they are forms, thus accelerating pyrolysis.

The primary liquid product from this process was designated “PyroOil” of which a distillation curve, below, is compared with some standard diesel fuel specifications. Note that the red line does not extend to 100% distilled, simply because the standard test procedure used only distilled up to about 350ºC, so that the heaviest 8% of the samples were simply reported as “residue.” This material had, however, left the reactor as a vapor or mist, before condensation and recovery by a spray wash step. Other sources report laboratory data showing heavier pyrolysis products from rubber continuing up to 600ºC and beyond. Most of 6.2% light HC product could be re-absorbed into the PyroOil stream, to raise the lower end of its BP curve closer or into the diesel range. (An alternative analysis of this product cut, of uncertain provenance, showed nearly twice the amount of light HCs.)

Aston University Bioenergy Research Group

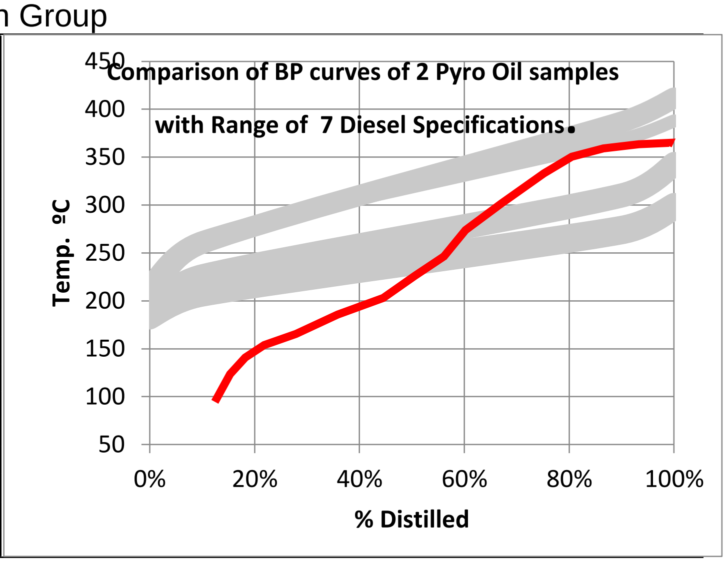
YIELDS FROM DRAG CHAIN PYROLYSIS REACTOR. (Average of 5 runs, for 30+ hours.)

Feed Rate	437 kg/hr
Nominal Temperature	600 ºC 1110 ºF
Yields	
Solid Carbon (1)	38.4%
Unreacted Rubber	4.4%
"PyroOil " Product (2)	38.6%
Light Condensibles (3)	5.2%
Non Condensible Gas	12.2%

(1) Mostly as coarse discharge from reactor, with possibly 40% as dust recovered from . condensible pyroOil product.

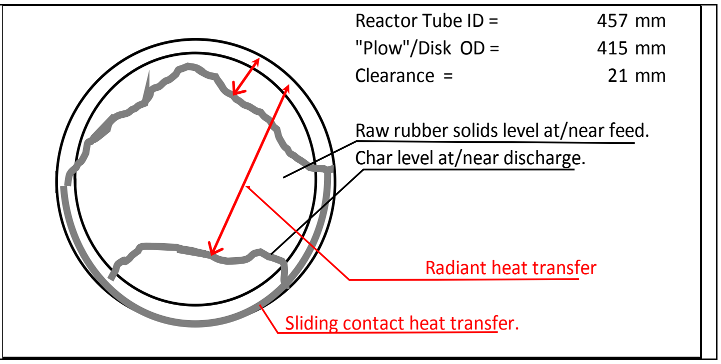
(2) Hydrocarbon mixture, approximating heavy diesel or light fuel oil.

(3) Hydrocarbons in C5 to C9 boiling range.



This process, at startup, was not heavily instrumented. The reactor exhaust temperature, for the combined streams from the upper and lower tubes, was held to 450ºC, and thus assumed to be average temperature throughout the reaction zone. The average reactor wall temperature, based on a single thermocouple was reported as 600ºC. The “plows” along the chain are of a proprietary design to maximize turnover of feed in temporary, direct contact with the hot wall. So this makes it an intermittent “fast” pyrolysis process, according to the definition table above. Most of the particles, most of the time, however are being slowly heated to roughly 450ºC, by hot gasses and adjacent products, which makes it predominantly a “slow” pyrolysis process. But this leaves at least 8% of the “fast” vapors, of BPs up to 600ºC, in a 450ºC environment, where naturally they condense as a sticky mist.

As sketched here, there is no direct contact between the “plows” and the vessel wall, there being a 2.3 cm gap, to avoid abrasive wear. Heat to the flowing solids is by radiation from above, or by direct sliding solid-to-solid contact, as material is pushed or “mashed” along the surface When the process was shut down, the upper parts of the wall were found coated with a porous charcoal layer, up to 2.3 cm thick.



Proximate analysis of this layer showed an extremely low ash level, well below that of either raw shredded tire feed or product carbon! This tells us that it was formed by the high-boiling mist or vapors, contacting the hot surface and continuing pyrolysis, leaving the carbonaceous deposit. (This is analogous to overflowing food baking onto stove or oven surfaces.) Because this layer was porous, it is thermally insulating, thus essentially precluding radiant heat transfer from the upper surfaces of the reactor. This leaves sliding solid contact as the essential means of heating the moving solids. At the feed end of the reactor, the cross-section is nearly full, of coarsely shredded rubber, as sketched above, with maximum wall contact. By the discharge end, the volume is reduced, by roughly 10x, so that this remaining char is in direct contact with a smaller area of the hot wall more of the time than earlier in its progress thru the reactor.

For this reactor alone, apart from the entire process, not shown, a rough emergency indicated a closure of about 87%. Because of very well-done insulation, combined losses plus heat of reaction, were thus 13% of the heating value of the raw tire feed. Since input heat was provided by the non-condensable fuel gas product, the overall process energy efficiency is even higher, which is fairly impressive compared with gasification processes, where .

As of sometime in 2016, the process had proven operable for up to around 90 days, with shut down usually due to massive agglomerations of dust and tarry solids, plugging the discharge area, between the reactor and a subsequent spray quench, not shown. This an example of a consistent problem in pyrolysis and gasification processes: Any vapor products of boiling points higher than that of the hot gasses carrying them will condense to a mist, and adhere to pipe or vessel walls, or agglomerate the inevitable dust particles in the stream. This potential problem will persist until the first point of contact with a cooling stream of quench liquid. Keeping the product stream hot enough to avoid this, will require larger streams of quench liquid, which may be any combination of recycled leavy liquid product and/or water. Cooling the product vapors before contact with a spray quench stream runs a high risk of heat exchanger tube fouling. The severity of this problem will vary substantially with the properties of the condensable product.

Epilogue

For any application there are various and often very different design concepts available that:

- Are demonstrated to be workable; meaning operational and economically viable
- Are claimed to be workable and possibly are
- With more development funds might be workable
- Consists of a patent and preliminary design.

If one is looking to buy a gasifier or pyrolyzer for a specific application, the “best” selection – aside from all technical considerations - is one for which the provider/seller/builder –

- Can offer a warrantee to cover any required modifications to keep the unit operable, for some specified period after startup.
- Has a technical staff to provide warrantee service within quick geographical reach.
- Has sufficient other projects or other related business activity to indicate that they will probably remain in business at least through the warrantee period.

If an engineer is tasked to do an evaluation or preliminary design for estimation of a process presented as “workable,” for purposes of potential purchase or investment, some questions that must be answered are –

- Is it in commercial or at least pilot scale operation anywhere?
- Has it been tested by pilot or prototype scale operation?
- How long has a unit been in continuous operation? (Preferably for multiple production runs.)
- Why was it shut down?
- Where’s the operating data?

If one has an idea for a novel, innovative design for a superior gasifier or pyrolyzer, and has funding to design and build a test unit “from scratch”.