Nordhausen, 17.08.2021

Process evaluation
Evaluation of "Duplex-TEC-Process®" from a chemical and process engineering point of view

Object:	Duplex-Turbulent-Expansive-Carbonbed-Process (Duplex-TEC-Process®)
Client:	TCP Energies GmbH & Co. KG Sellierstraße 1 07745 Jena
Order nr.:	1AU-228313 / 1AU-261490
Consignee:	TÜV Thüringen e.V. Melchendorfer Str. 64 99096 Erfurt
Inspector/expert:	Dipl.-Ing. W. Timaeus, Dipl.-Ing. (FH) J. Hentrich

The process evaluation includes 20 pages.

1. Task

The TCP Energies GmbH & Co. KG Jena commissioned the TÜV Thüringen e.V. with the evaluation of a process, developed by TCP, for the gasification of high-calorific waste from a chemical and process engineering point of view. The aim of the process is to generate electrical energy by using the gas produced in turbocharged gas engines or to generate heat.

Furthermore, the results of the test series at the pilot-/pre series plant (full scale 1:1) at the location Schöngleina, Thüringia/Germany between 1998 and 2011 are rated.

A plant-specific and device-specific evaluation of the so-called “Duplex-Turbulent-Expansive-Carbonbed-Process (Duplex-TEC-Process®”) is not done.

2. Documents used

For the preparation of the process evaluation in the period between 12.07.2021 and 23.07.2021 the following documents have been made available to TÜV Thüringen e.V. by TCP Energies GmbH & Co. KG.

- The document „Basics of gasification – Multi-stage waste gasification using Duplex TEC-Process, Streitenberger 2020“ by TCP Energies GmbH & Co. KG
- The documentation of pilot-/pre-series plant based on Duplex-TEC-Process® in operation between 1998 and 2011, Location: Schöngleina, Thuringia/Germany by TCP Energies GmbH & Co.KG
- A schematic representation of input- and discharge situation within thermal range, status: 07.2021
- A PDF-file „Supplements within the scope of the obligation to cooperate 21.04.pdf“ with the following declarations:
  - Proof of 98% Carbon conversion based on Duplex TEC-Process®
  - Exact reaction equations with boundary conditions (temperature, pressure and others)
  - The calculation of the efficiency factor
  - Designation of the installed measurement equipment in reactor and gasifier
  - Other relevant process engineering data and boundary conditions
  - Calculations for material, energy and mass balance based on Duplex TEC-Process® procedure - accounting for a TCP WGL 1-30, status 30.03.2018 variant 57/43 by TCP Energies GmbH & Co. KG

3. State of the art

Definitions:

The process to be evaluated for the gasification of high-calorific waste is determined and named by the developer TCP Energies GmbH & Co. KG as Duplex-TEC-Process®.

Gasification is the thermal conversion of carbon-containing substances into a product gas, which mainly consists of carbon monoxide, hydrogen, methane and light hydrocarbons. Other ingredients are carbon dioxide, water and nitrogen depending on the process used.

„Cracking“ (derived from “to crack”) describes a process commonly used in petrochemistry in which longer-chain hydrocarbons are split into shorter-chain hydrocarbons using heat, pressure and catalysts.

In the present process assessment, the terms pyrolysis and thermolysis are used as follows:
Pyrolysis: thermal conversion of input materials **without** using gasification agents;
Thermolysis: thermal conversion of input materials **using** gasification agents.

Procedure:

Pyrolysis of solid substances:

Pyrolysis is a process of thermal cleavage of chemical compounds, whereby temperature forces breaking of bonds within large molecules. In contrast to gasification this usually takes place excluding oxygen in order to prevent combustion.
Pyrolysis usually takes place at temperatures above approximately 350°C, in the case of organic waste the existing hydrocarbon chains are cracked into shorter chain molecules.
Within *Pyrolysis* coke, oil and gas can be extracted. At low temperatures there is a higher oil content, at high pyrolysis temperatures the gas content increases.
Pyrolysis runs endothermic. Due to the lack of combustion the required process heat is supplied from the outside. [1]

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gasification of solid substances:

The basic principle of gasification is determined by the incomplete combustion of the fuel used. Gasification usually takes place at temperatures higher then 500°C. Today's gasification systems usually work with temperatures between 850 - 1,200°C, processes up to 2,000°C are also known.
The incomplete combustion is caused by an insufficient supply of oxygen to the combustion process.

The hydrocarbon compounds will be completely broken down and will, by attaching of oxygen, ideally be split into carbon monoxide and hydrogen.
In principle, the gasification process is exothermic, heat energy is released.
The energetic efficiencies in gasification processes lies between 80 and 95%, depending on the type of gasifier and process control. [1]

<u>Plant engineering:</u>

The thermochemical conversion of solid fuels into a fuel gas takes place in the gasification reactor (gasifier). Upflow and downflow gasifiers are mainly used in small plants. The order of the conversion steps of solid fuels, such as drying, pyrolysis, partial oxidation and reduction depends on the type of gasifier used.
With its chemical, mechanical, caloric and reaction-kinetic properties, the fuel determines the selection of the apparatus suitable for the respective process. Furthermore, the required power is a crucial parameter.
In the constructive solution, specific process parameters like pressure and temperature have to be taken into account. Usually, a shaft apparatus as well as fluidized bed apparatus and combinations of these are used for the gasification of solid fuels [2].

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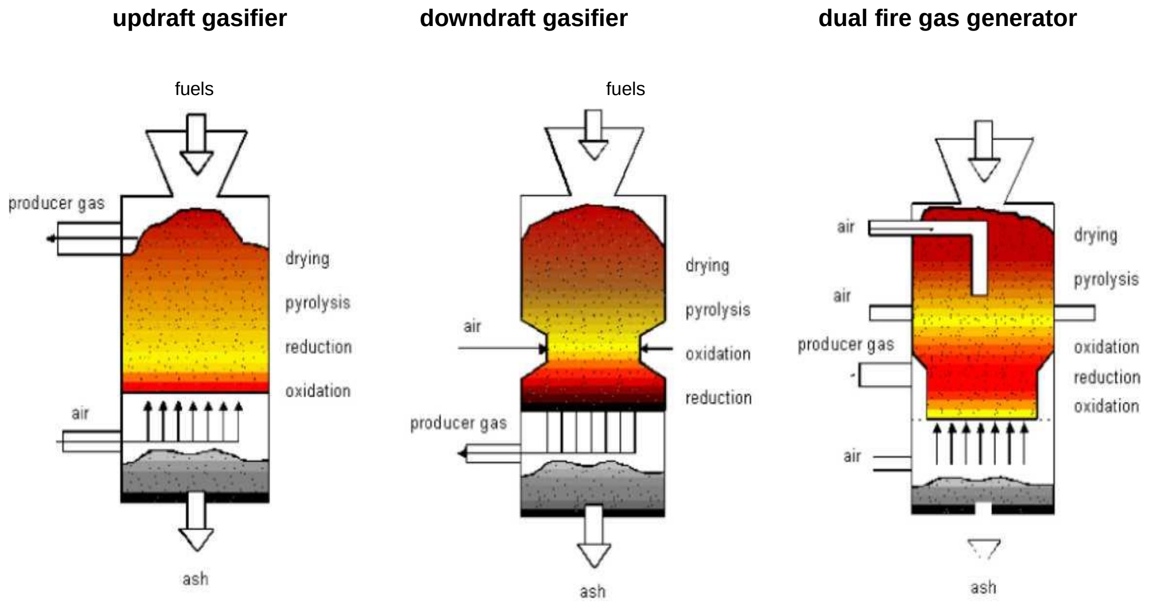

Illustration 1: gasifier variants

Concepts in which different areas are physically separated from each other, especially pyrolysis from oxidation, have been developed and implemented primarily in recent years. Optimizing each step and minimizing tar production are the main reasons for this separation [3].

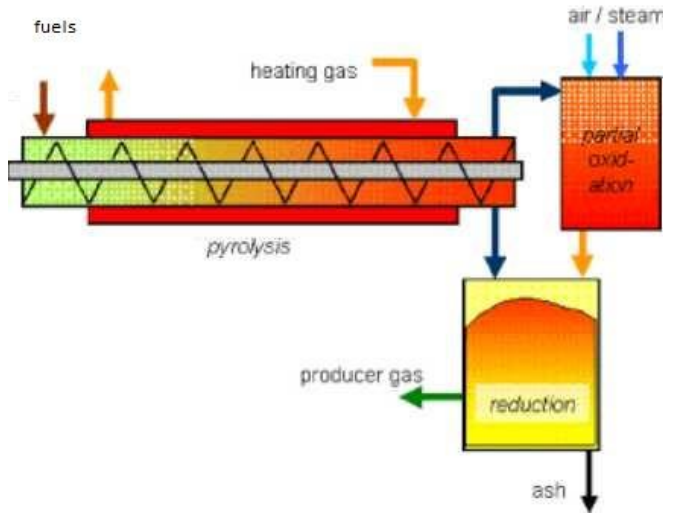

Illustration 2: Two-stage gasifier

4. Chemical reaction

The lack of oxygen is characteristic of the chemical processes during gasification (λ < 1), in contrast to combustion with excess oxygen (λ > 1). Via several chemical reactions the conversion of the bound carbon and hydrogen into the main raw gas components CO, CO_2, H_2, H_2O and CH_4 is initiated Heterogeneous reactions of the gasification agent respectively of the product gas with the solid (R2, R3, R5, R6, R8) are taking place. Furthermore homogeneous reactions between reaction products as well as with the gasification agent in the gas phase (R1, R4, R7, R9) and pyrolysis reactions of the solid (R10, R11) are taking place.

Table 1 **Reaction equations of carbon gasification [4/5]**

Reaction equation			ΔH_{298} [kJ/mol]	description	
$H_2 + ½O_2$	⇄	H_2O	-242	combustion	R1
$C + O_2$	⇄	CO_2	-406	combustion	R2
$C + ½O_2$	⇄	CO	-123	partial combustion (incomplete)	R3
$CO + ½O_2$	⇄	CO_2	-283	partial combustion	R4
$C + CO_2$	⇄	2CO	+160	Boudouard-reaction	R5
$C + H_2O$	⇄	$CO + H_2$	+119	heterogeneous water gas reaction	R6
$CO + H_2O$	⇄	$H_2 + CO_2$	-42	homogeneous water gas reaction	R7
$C + 2H_2$	⇄	CH_4	-87	hydrogenating gasification	R8
$CO + 3H_2$	⇄	$CH_4 + H_2O$	-205	methanation	R9
CH_xO_y	⇄	$(1-y)C + yCO + x/2H_2$		pyrolysis	R10
CH_xO_y	⇄	$(1-y-x/8)C+yCO+x/4H_2+x/8CH_4$		pyrolysis	R11

The information in Table 1 clearly shows that the product gas composition depends on the **gasification agent and the process control**. Thus, CO2 is used as a gasification agent for the formation of CO (R5), while water vapor is used in the production of water gas (R6). Since both reactions are endothermic, an energy supply is required. This can be done externally by means of

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allothermic gasification or by partial combustion (R3) in the reactor itself as autothermal gasification [5].

5. Process technology

Since gasification is a process in which the solid is converted into a fuel gas in a thermochemical process, the addition of a reaction gas is absolutely necessary. Depending on the target specification for the process and the desired quality of the product gas, reaction gases such as air, oxygen, steam, carbon dioxide or mixtures of the mentioned gases are used.

For economic reasons in most cases air is used as the gasifying agent in order to generate electricity and heat. Moreover there a methods and systems known in which water steam is used. The use of air or oxygen-containing gasification agents brings the advantage that the process runs autothermal, since the temperatures required for the endothermic gasification reactions are provided directly from the process by the exothermic oxidation reactions.

The sub-steps of the reaction process in the gasification of solid fuels can be divided into drying, degassing, reduction and gasification/combustion. If several goals are aimed at in just one reaction room, the individual zones in which the sub-steps take place are insufficiently separated from one another. As a result, optimization with regard to the conversion of the solid and the adjustment of the gas quality through the process control are difficult, since targets and influencing variables often overlap and thus inhibit.

The possibilities of influencing the process in a targeted manner by controlling the most important influencing variables are presented with the description and analysis of the procedural basics of the gas generation process.

The relevant influencing variables are:

- properties of the input material
- oxygen supply
- Dwell time
- temperature
- pressure
- additives
- required quality of the product (fuel gas)

[2].

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Depending on the properties of the solids to be converted and the process and apparatus used, appropriate conditioning must be carried out before the thermal conversion process.

Above all, a high water content of the solids has a negative effect on the efficiency of the thermal process. For the gasification, values between 10% and 15% are specified as the optimum input water content for the solid fuels [2].

For the most part, the upstream pyrolysis is carried out in rotary kilns which have been well-known for more than 50 years. Here mixing takes place as a result of the rotary movement.

As already mentioned under point 3, plant concepts have been further developed in which the various stages of converting solid fuels into usable combustible gas, such as drying, pyrolysis/thermolysis are used, They present the current state of the art.

In terms of apparatus technology, an assembly with an upstream stage for drying the fuel, followed by a thermolysis and a subsequent staged gasification with spatially separate partial oxidation and reduction represents a new state of the art.

A major advantage of pre-gasifier thermolysis is baed on the fact the fuels are not getting into contact with combustion gases during thermolysis. [6]

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6. Evaluation of the procedure

6.1 Description of the procedure

From a procedural and plant engineering point of view, the Duplex-TEC-Process® (Duplex-Turbulent-Expansive-Carbonbed-Process) represents a multi-stage closed thermal waste treatment of carbonaceous waste of high energy content to produce gas for subsequent electricity and heat generation.

The assembly consists of drying, degassing/ smoldering (referred to as thermolysis in this process) and a gasification step. The three processes are coupled, among other things, in terms of flow and heat and are separated spatially and in terms of equipment.

The pre-gassing and the main gassing will be evaluated at this point.

In the dryer, the processed raw material will be pre-dried to residual moisture content of approx. 10 – 15 % water and fed automatically and continuously to the pre-carburetor. In the pre-gasifier, the input material is heated to average temperatures of approximately 350 – 500 °C with the addition of recuperatively preheated and oxygen-enriched air. Under controlled operating conditions such as pressure, temperature, gasification agent supply, heating and retention time the conversion to carbon coke, tar/ oil and low-temperature carbonization gas takes place in the various temperature zones of the reactor. In this process, the residual moisture is evaporated and the organic compounds are converted into low-temperature gas and carbon.
Without interruption and spatial separation the carbon coke, consisting of low-temperature carbonization gases, water vapor and other various gas components is fed directly into a special multi-stage gasifier in an ascending direct current/ entrained flow.
The first stage of the lower part of the gasifier consists of a carbon tray (area of the lower main gasifier part, where the carbon mixture (solid content) from the pre-gasifier is fed into the main gasifier from the side) with a partial perforated base and centrally moving mixing tools. Here the carbon coke is fed in and flown through by a hot, pre-stressed gasification agent. The mixing tools placed in the carbon-coke bed result in gassing, mixing and stirring, and thus comprehensive wrapping of the carbon particles. When the gasification agent and the associated reactive gas compounds (hot spots) are fed in, a quasi-fluidized and floating turbulent-expansive carbon bed (turbulent-expansive carbon bed) with voluminous expansion (floating) of the same occurs.

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Simultaneously feeding the low-temperature carbonization gases from the preliminary process directly into the moving carbon bed leads to associated oxidation-reduction reactions at temperatures of ≥ 800 °C and thus to the thermochemical breakdown of the molecular carbon compounds to form gaseous components.

From a procedural assessment, it can therefore be assumed that the available carbon particles are almost completely gasified.

In the second stage, in the oxidation-reduction space above the fluidized carbon-coke bed, a further thermochemical conversion of the carbon particles entrained upwards in the entrained flow takes place at temperatures of circa 1200°C to 1300°C.

In the third stage, the gas-residual carbon mixture flows turbulently through partial flow channels into the oversized (compared to the oxidation-reduction space in the second stage) post-reduction room.

If the retention time is sufficient, the residual coal dust is completely converted into a combustible, tar-free process/ fuel gas.

The resulting process/ fuel gas, essentially consisting of CO, H_2, CH_4, CO_{que} and minimal residual dust, is extracted in the upper part of the gasifier and subjected to a multi-stage cleaning and cooling process. This takes place in a special heat exchanger cyclone, a subsequent heat exchanger, a hot gas filter and a gas quench for rapid cooling of the hot gas.

6.2 Chemical reactions

According to the presented process description, the Duplex-TEC-Process® is based on the following chemical reactions:

Table 2 **Reaction equations of carbon gasification on which the Duplex-TEC-Process® is based**

Reaction equation			description	reaction, acc. chapter 3
$C + O_2$	$\rightarrow$	CO_2	oxidation	R2
$C + CO_2$	$\rightarrow$	$2\ CO$	Boudouard reaction	R5
$C + H_2O$	$\rightarrow$	$CO + H_2$	water gas reaction	R6
$C + 2H_2$	$\rightarrow$	CH_4	methane formation	R8
$CH_4 + H_2O$	$\rightarrow$	$CO + 3\ H_2$	methane reforming	
CH_hO_o	$\rightarrow$	$\frac{2}{3}CO + \frac{1}{3}CH_4 + (o - \frac{2}{3})H_2O + (^h/_2 - o)H_2$ thermal tar decomposition - hypothetical reaction equation		--
$CO + \frac{1}{2}O_2$	$\rightarrow$	CO_2	carbon monoxide oxidation	R4
$H_2 + \frac{1}{2}O_2$	$\rightarrow$	H_2O	hydrogen oxidation	R1
$CH_4 + {}^3/_2O_2$	$\rightarrow$	$CO + 2\ H_2O$	methane partial oxidation	--
$CH_hO_o + \frac{1}{2}O_2$	$\rightarrow$	$CO + oH_2O + (\frac{1}{2} - o)H_2$	tar partial oxidation	--
$CO_2 + H_2$	$\rightarrow$	$CO + H_2O$	homogeneous water gas reaction	R7

The chemical reactions are largely matching with the reaction equations for carbon gasification described in the literature [4/5/8]. The temperature ranges which are required that the reactions take place are present in the reactors described.

However, it cannot be proofed that all reactions will take place exactly in the same way within the two reactors and gasification stages. The processes of methane reforming and thermal tar decomposition or partial tar oxidation are questionable.

In conventional methane (steam methane reforming or SMR: $CH_4 + H_2O \rightleftarrows CO + 3\ H_2$) reforming, the methane is converted into carbon monoxide in a reformer at a temperature of 800 to 900 °C and a pressure of around 25-30 bar over a nickel catalyst with water. Under atmospheric conditions, methane reforming is only of significant importance in the presence of catalytically active solids, which may include bed ash or bed material.

However, as early as 2002, a process was described in which a hydrogen-rich (44 %) synthesis gas with a very low methane content (1 %) was produced by so-called "staged reforming" [7]. In staged reforming, pyrolysis and gasification are technically separated from each other.

Based on the analyzes of the fuel gas in the documentation "TCP WGL - documentation of the first fuel gas plant in operation between 1998 and 2011", which show a proportion of higher hydrocarbons < 0.1 % in campaigns 14-15 and 28-29, it can be assumed that the tar components produced in the pre-gasifier are converted in the multi-stage main gasifier.

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6.3 Process technology

The thermolysis takes place in the pre-carburetor, a closed, stationary reactor with an autothermal process control with gasification agents and internal conveying devices. These devices are primarily used to transport the fuel and less to mix it since the firebed should remain in the reactor. This reactor differs significantly from the well-known (rotary kiln) pyrolysis / thermolysis which takes place in hermetically sealed, indirectly heated rotary kilns [9].

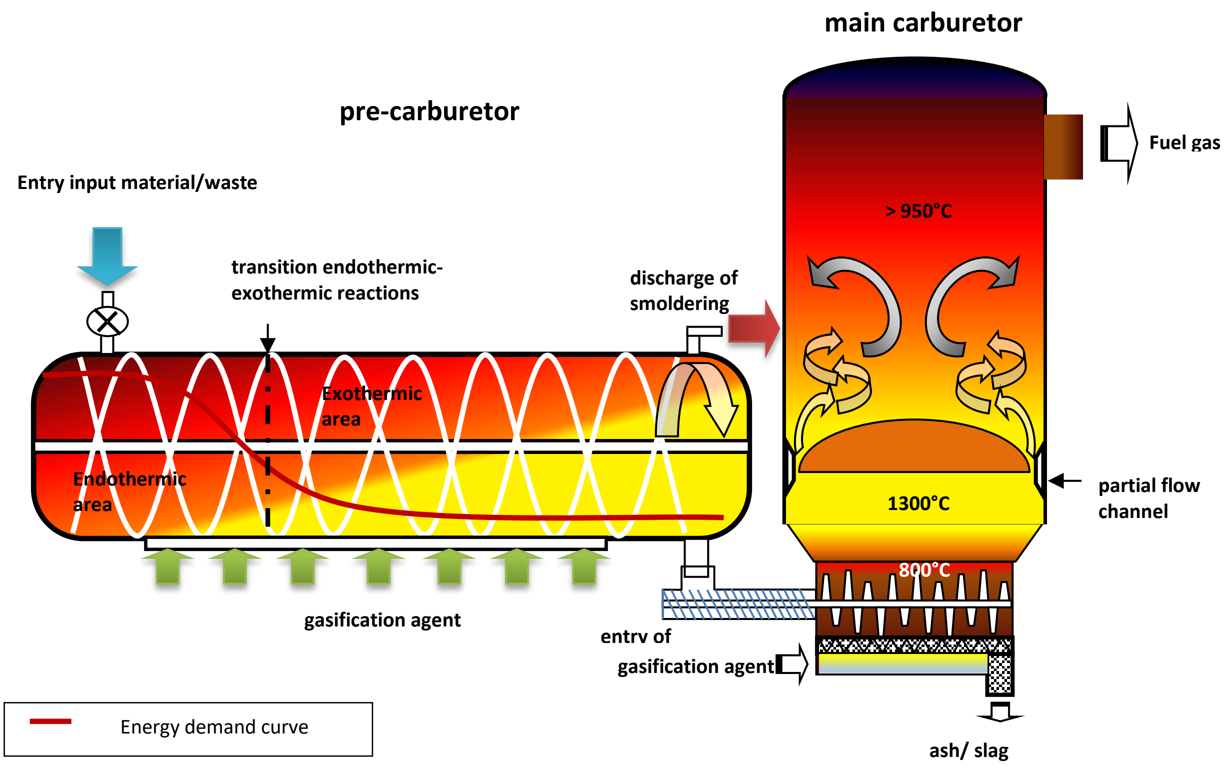

Illustration 3: Schematic representation of pre-gasifier and main gasifier of the Duplex TEC Process

The Duplex TEC (Turbulent Expansive Carbonbed) multi-stage carburetor is designated as main gasifier. It is an ascending combination of a coflow gasifier and an updraft gasifier. The gas-conversion takes place through adaptive gasification stages (by special fluidic installations) and a fluidized-floating turbulent-expansive carbon bed. This multi-stage design combines the advantages of a fixed-bed gasifier with an ascending gasification as well as a fluidized-bed gasifier, a stationary fixed bed and an upstream gasifier.

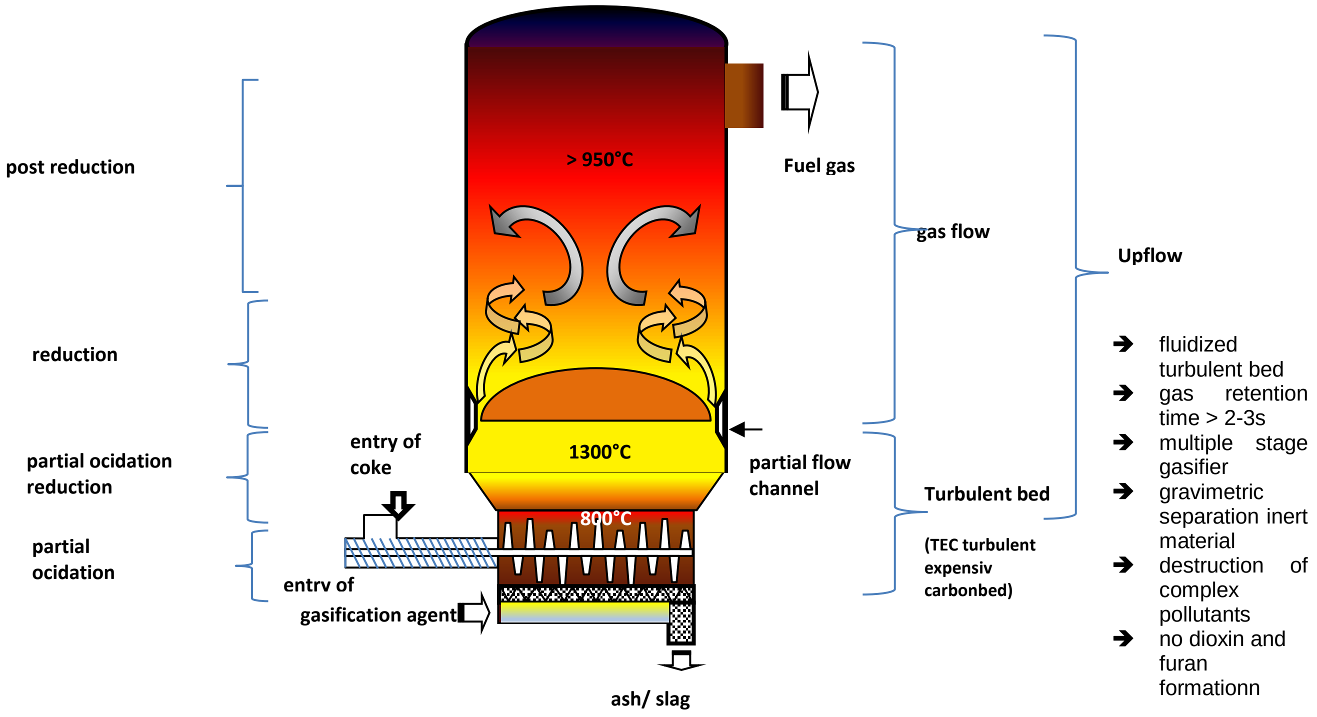

Illustration 4 : Main carburetor (Duplex TEC multi-stage gasifier)

In this main carburetor, the precisely metered volume flow of gasification agent (air - oxygen mixture with an O_2 content > 50 %) causes the fixed bed (semi floating bed) to be fluidized in the first stage. A thermochemical conversion of carbon to a raw gas with high energy content takes place in the spatially limited stationary fluidized bed.

By mixing the carbon bed with the gasification agent supply via a perforated plate and destroying the capillary formation with a stirring tool, almost complete carbon conversion can be achieved.

A so-called oxidation-reduction space is located in the bell-shaped partition to the post-reduction space above the fluidized carbon bed. It applies constant radiant heat to the released gases and dust at a temperature of approximately 1200 °C -1300 °C. The bottom to top material flow triggers redox reactions in this zone.

The mass transport into the post-reduction space above is realized via an annular slot between the partition wall and the reactor wall.

This post-reduction space (> 950 °C) above the bell-shaped partition with specific gas flow and sufficient free gasification space (entrained flow) intensifies the gasification process to such an extent that long-chain organic compounds are largely destroyed and broken down into low-molecular components. Due to the existing volume of the free gasification chamber, a retention time of >2-3 s shall be achieved and the remaining tar fractions should be almost completely converted during this time. The sediment discharge is expected to be small.

The entire system is operated at low pressure. Measures for explosion protection are therefore minimized.

For process control and monitoring, O_2 sensors for measuring the oxygen concentration, thermocouples for temperature monitoring and pressure sensors for monitoring the pressure regime are installed in the pre-gasifier and in the main gasifier.
A radiometric measurement provides the control of the fluidized fixed bed in the main gasifier.
After quenching the gas, the product gas quality is monitored by a gas analysis equipment.

The presented material flow analysis, the material, energy and mass balance, the calculation of the efficiency and the process modeling are largely comprehensible.

7. Summary

By separating the three treatment stages of drying, degassing/ smoldering, referred to as pre-gassing (thermolysis) in this process, and main gassing, the optimal and required process conditions can be set in each stage.
This creates a decisive prerequisite for the high utilization of the energy content of the high-calorific input and waste materials used for the production of a fuel gas, suitable for thermal and/ or electrical use.

In connection with the subsequent use of the released process heat and the heat that arises when generating electrical energy using gas engines, the process can achieve even greater efficiency. This can be further increased by using ORC systems (Organic Rankine Cycle) to generate addtional electricity.
The evaluated process represents a new development due to the staged autothermal gasification using a fluidized turbulend bed in the cocurrent process (ascending) and a sufficiently large post-reduction chamber. Thus the process corresponds to the state of the art.

A basis for process modeling was created due to the extensive and documented research on the pilot pre-series assembly on industrial scale during the period of 2000 to 2011. The experience gained can be implemented directly in the construction of industrial assemblies. The actual assembly size must not change. Rather larger plants are to be implemented in a modular manner by using several assembly modules operated in parallel (Waste Gasification Lines - WGL®). This prevents errors in up-scalling.

Based on the documents handed over to us and the literature research, it can be concluded that the Duplex-TEC-Process® developed by TCP Energies GmbH & Co. KG Jena, is suitable from a chemical-process engineering point of view for the gasification of high energy input materials/ waste.

We assure that we have prepared this process evaluation impartially and to the best of our knowledge and belief.

The process evaluation is available in two copies. The client receives one copy, one remains with our documents.

Dipl.-Ing. Wulf Timaeus
Head of department industrial service

Dipl.-Ing. (FH) Jörg Hentrich
Expert steam/pressure technology

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8. Credits

[1] http://www.ikr-schalles.de/Die_Vergasung_organischer_Abfalle.pdf

[2] Böhning, D.; Beckmann, M.: Vergasung und Verbrennung von Biomasse für den dezentralen Anwendungsbereich. In: Energetische Nutzung nachwachsender Rohstoffe. 19. Fachtagung, 17.09. - 18.09.2013 in Dresden

[3] Leitfaden für die sichere und umweltverträgliche Biomassevergasung, Deutsche Version, November 2009

[4] https://campus.tum.de/tumonline - Prozesstechnik_Kapitel5.pdf

[5] http://diglib.uni-magdeburg.de/Dissertationen/2003/eycschotte.pdf: Untersuchungen zur Vergasung und Verbrennung von Kohlen und Biomassen unter Anwendung der Gaspotentiometrie mit Sauerstoff-Festelektrolyt-Sonden

[6] EP0522919 (A1) - Process and installation for the thermolysis of industrial and/or domestic waste (http://worldwide.espacenet.com)

[7] Michael Mayer, Heinz-Jürgen Mühlen und Christoph Schmid 2002: Gestufte Reformierung biogener Reststoffe - Erste Betriebserfahrungen. Präsentation auf der DGMK Tagung "Velen V"

[8] https://www.yumpu.com/de/document/view/2740784/zur-vergasung-von-rest-otto-von - guericke-universität-magdeburg/91: Zur Vergasung von Rest- und Abfallholz in Wirbelschichtreaktoren für dezentrale Energieversorgungsanlagen – Dissertation zur Erlangung des akademischen Grades Doktoringenieur (Dr.-Ing.) von Dipl.-Ing. Helmar Tepper

[9] http://www.dgengineering.de/Drehrohr-Verfahren-Pyrolyse.html