

LIGNITE CHEMICAL CONVERSION IN AN INDIRECT HEAT ROTARY KILN GASIFIER

by

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The results on the gasification of Greek lignite using two indirect heat (allothermal) pilot rotary kiln gasifiers are reported in the present work. The development of this new reactor-gasifier concept intended for solid fuels chemical conversion exploits data and experience gained from the following two pilot plants. The first unit A (about 100 kg/h raw lignite) demonstrated the production of a medium heating value gas (12-13 MJ/Nm³) with quite high DAF (dry ash free) coal conversions, in an indirect heat rotary gasifier under mild temperature and pressure conditions. The second unit B is a small pilot size unit (about 10 kg/h raw lignite) comprises an electrically heated rotary kiln, is an operation flexible and exhibits effective phase mixing and enhanced heat transfer characteristics. Greek lignite pyrolysis and gasification data were produced from experiments performed with pilot plant B and the results are compared with those of a theoretical model. The model assumes a scheme of three consecutive-partly parallel processes (i. e. drying, pyrolysis, and gasification) and predicts DAF lignite conversion and gas composition in relatively good agreement with the pertinent experimental data typical of the rotary kiln gasifier performance. Pilot plant B is currently being employed in lime-enhanced gasification studies aiming at the production of hydrogen enriched synthesis gas. Presented herein are two typical gas compositions obtained from lignite gasification runs in the presence or not of lime.

Key words: *indirect heat (allothermal) rotary kiln gasifier, pilot plant, gasification modeling, lime enhanced gasification, Greek lignite*

Introduction

The main objective of *Clean Coal Technologies* (CCT) is coal exploitation for power and heat production by using processes that maximize the overall efficiency and diminish emissions of hazardous wastes and greenhouse gases. *Coal Gasification Technologies* have many positive attributes, compared to other CCTs. Gasification is the only advanced CCT that offers both upstream (feedstock flexibility) and downstream (product flexibility) advantages. All carbon-containing feedstocks including hazardous wastes, municipal solid waste and sewage sludge, biomass, *etc.*, can be readily gasified after proper preparation to produce clean synthesis gas for further processing. Due to the pos-

sibility of processing use low-cost feedstocks, gasification is the technology of choice for many industrial applications, *e. g.* oil refineries. *Integrated Gasification Combined Cycle* (IGCC), and gasification processes in general, is also the only advanced power generation technology capable of co-producing a wide variety of commodity and premium products, in addition to electricity [1].

Compared to combustion systems, gasification is the most efficient and environmentally friendly technology for producing low-cost electricity from solid feedstock and can be made to approach that of natural gas combined cycle plants. Further increases in efficiency can be achieved through integration with *fuel cells* and other advanced technologies. Because gasification operates at high-pressure in a reducing atmosphere, gasification products compared to direct combustion products are more amenable to cleaning to reduce ultimate emissions of sulfur and nitrogen oxides, as well as other pollutants. In general, the volume of the fuel gas processed in an IGCC plant for contaminant removal is typically one-third that from a conventional power plant. Gasification plants can also be configured to reach near-zero levels of emissions when required.

The present work aims at the development of a new type of gasifier (rotary kiln) to process low heating value coals (*e. g.*, moist lignite) for the production of synthesis gas free of nitrogen and combustion by-products (medium heating value gas – MHV gas). The focus is on the following aspects: (1) Generation of experimental data from gasification test on Greek lignite. Main results concern DAF lignite conversion and product gas composition. (2) The validation of a coal conversion model with particular emphasis on moist lignite gasification. The model, as explained in the relevant paragraph below, utilizes kinetic correlations for coal drying, pyrolysis and gasification. The pertinent citations are provided where appropriate. As far as the kinetics and product distribution for lignite pyrolysis, the model proposed by Merrick [2] was adopted, whereas the Johnson's kinetic model of lignite gasification was incorporated in mass and enthalpy balances [3].

Apart from the kinetic correlations thermodynamic analysis for the gasification system offers obvious advantages in case chemical equilibrium is ascertained. Recent publications elucidate the various thermodynamic aspects and report gas composition predictions for specified gasification systems, where solid fuels are involved (*e. g.*, lignite, coal, biomass, or solid wastes with or without additional sorbents (*e. g.*, lime) for CO₂ capture) [4-6].

A review of characteristics and limitations of conventional gasifiers is summarized in tab. 1, to enable comparisons with the novel type of gasifier.

Selection of gasifier: the indirect heat rotary kiln

Gasification of low quality solid fuels: reactor type selection criteria [7]. A number of criteria should be set for selecting a gasification reactor type to be integrated in a process efficient enough to compete successfully processes involving conventional coal conversion reactors.

Table 1. Synthesis gas composition (% v/v) and HHV from pilot plant A [17, 22]

Process designation	H ₂	CO	CO ₂	CH ₄	N ₂	H ₂ S	HHV* [MJ/Nm ³]
ALKIGAS ⁽¹⁾	35-46	24-47	15-22	4-8	–	0.0-0.8	10.3-13.8
MBG process ⁽²⁾	51.11	12.26	24.04	11.80	0.48	0.32	11.4
LURGI ⁽³⁾	36-40	18-25	27-32	9-10	–	–	11.5
– use of air	6.0-6.7
WINKLER ⁽⁴⁾	35-45	30-50	13-25	0.5-2.0	–	–	9-13
– use of air	4.3-4.7
KOPPERS-TOTZEK ⁽⁵⁾	22-32	55-66	7-12	0.1	–	–	10.6-11.8

* HHV – higher heating value

Process operating conditions

- (1) ALKIGAS (pilot plant A of this work): atmospheric, 900-950 °C, use of air, allothermal, feed – raw Greek lignite (Megalopolis), $d_p = -15$ mm, max moisture 60% w/w
- (2) MBG process (under development): fluidized bed, allothermal, pressure 40 bar, max temperature 1000 °C, feed – gasing coal from the Northern part of the Ruhr region (Germany) [33]
- (3) LURGI (commercial): fixed bed, autothermal, use of O₂ + steam, pressure 20-30 bar, lignite feed, $d_p = 6-40$ mm, max moisture 15% w/w
- (4) WINKLER (commercial): fluidized bed, autothermal, use of O₂ + steam, atmospheric pressure, lignite feed, $d_p = -40$ mm, max moisture 18% w/w
- (5) KOPPERS-TOTZEK (commercial): auto-thermal, use of O₂ + steam, atmospheric pressure, feed – any type, $d_p < 0.1$ mm (powder), max moisture 18% w/w, temperature 1110-1480 °C

General criteria

- *The process overall should include the simplest possible flowchart, comprise proven process units and allow for high operation availability, since this factor weighs heavily on process economics.*
- *The process should provide the flexibility of processing solid fuels of different type, origin and composition with minimum preparation treatment. This offers obvious benefit in the management of raw materials.*
- *Production of a medium heating value (MHV) gas should be possible without using oxygen, for the generation of the hot medium to heat up the gasification reactor. This requirement imposes the need of using indirectly heated (allothermal) process stages. Savings are to be expected by avoiding both the needs for an air fractionation plant and the processing of high gas mass flow rates in the case of having a low heating value (LHV) product gas, instead of a MHV gas. With regard to gasifier heating up, the allothermal mode of operation offers the flexibility of either producing heat from whatever clean fuel (*i. e.* different from fuel being gasified) or use available heat recovered from independent process units. Moreover, the MHV gas if it is to be used to fuel a gas turbine is expected to demonstrate superior combustion characteristics than an LHV gas.*

Criteria related to reactor characteristics

- *No particle size limitations either in the feed or during processing.* The reactor should operate with feeds composed of a mixture of lumped and pulverized material *i. e.* wide particle size distribution (*e. g.*, d_p –40 mm). Particle size reduction due to thermal treatment and particle attrition should not cause stoppage of solids motion through the reactor. Also savings are to be expected by reducing solids mechanical preparation.
- *Feed containing the full inherent moisture content.* The reactor should provide for the processing of feeds with any moisture percentage. In the case of raw lignite possessing with moisture over 50% the need for independent steam generation installation is overcome.
- *Reactor operation under a controlled atmosphere.* Reactor operation maintaining a controlled atmosphere offers several advantages. This type of operation is accomplished by applying an indirect mode of heating up whereas the obvious advantage is the generation of gas streams (*i. e.* steam, pyrolysis gas, synthesis gas) free of unburned air and combustion products.
- *Effectiveness of phase mixing and heat transfer.* Reactor design, internal configuration and operating conditions should enable an effective mixing of the reaction mixture for enhancing the mass and heat transfer rates between the reacting species.
- *Control of solids hold-up and residence time.* An effective reactor type should also provide for a stable and reliable control of the residence time of reactants at the desired level. Moreover reactor operation should guarantee a quick response for the transition from one steady state to another.
- *Operation at high temperatures and pressures.* Solid fuel gasification kinetics and thermodynamics are strongly dependent on operating temperature and pressure. Depending on the particular application it might be desirable to operate at reactor temperature well above 1100 °C and pressure over 30-50 bar.

Indirect heat rotary kiln is the type of reactor that meets more successfully the above-mentioned gasifier specifications, especially for gasifying moist lignite. However, it has to be mentioned that it is an atmospheric pressure gasifier operating at temperature below 1000 °C. This conclusion is justified in view of the various limitations encountered in the established gasification processes with respect to the above-mentioned criteria, with particular emphasis on that of allothermal gasification. Rotary kiln design and construction is relatively simple and the pertinent technology is established and reliable with industrial applications in the cement and metallurgical industry. Moreover, indirect heat dryers find important industrial applications in the production of sensitive dry solid products and/or clean steam whereas indirect heat calciners find also a variety of important industrial uses [8]. Industrial calciners can be at least 30 m long and 3 m wide [9, 10].

During the past two decades experimental and theoretical work on the gasification of Greek lignite in indirect heat (allothermal) rotary kiln gasifiers has yielded results that could be exploited for the implementation of scaling-up design to a demonstration, or a full industrial size. Process flow sheet, reactor-design equations, experimental results

and various design development aspects of this novel technology have already presented in several publications [7, 11-27].

Modeling an allothermal rotary kiln gasifier

An outline of a theoretical model simulating the allothermal rotary kiln gasifier operation for the chemical conversion of a solid fuel feedstock is presented. This is a useful theoretical tool for the interpretation and validation of the results to be obtained from the implementation of the lignite gasification experimental program. A full account of the gasifier modeling is reported elsewhere [11]. Literature kinetic correlations for the pyrolysis (devolatilization) [2] and gasification [3] of lignite have been incorporated in the mass and energy balances valid for steady-state gasifier operation. For the lignite drying process we employed a kinetic correlation originally deduced from TGA measurements [28] and subsequently verified from pilot drying tests carried out on our rotary gasifier (pilot unit B) under drying temperature conditions [12].

The gasifier model provides for a general scheme of three parallel processes (drying, pyrolysis, and gasification). In actual fact it turns out that the three processes progress according to a series-parallel scheme as the solids move along the kiln length and they gradually enter higher temperature regions of the kiln. Details of the gasification process scheme are schematically illustrated in fig. 1, where the partial overlapping between successive processes is pictorially represented.

The light and medium molecular weight volatile content being released from the fed solids upon heating over a temperature threshold typical for each solid exhibiting a

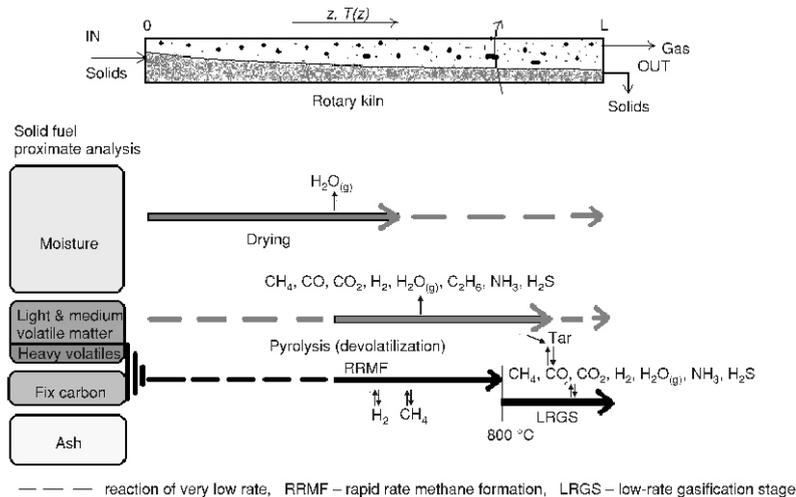


Figure 1. Schematic representation of processes occurring in an allothermal rotary kiln gasifier

specified composition is subjected to a gradual thermal decomposition (pyrolysis). At this stage at least nine chemical species are produced as follows: CH₄, CO, CO₂, H₂, H₂O_(g), C₂H₆ (as equivalent of all hydrocarbons with two or more carbon atoms), NH₃ (as equivalent of all nitrogenous substances), H₂S (as equivalent of all gas sulphurous substances) as well as tar [2]. The tar is composed of light organic substances *i. e.* those containing shorter carbon chains than the organic substances and it usually appears in the liquid or gas phase by taking account that at this stage a high temperature prevails.

The steam atmosphere is gradually enriched with the pyrolysis gaseous products and the gas-solids mixture continues to be heated. The thermal decomposition is paralleled by the RRMF (rapid reforming methane formation) [3]. However this reaction is favored by high pressure and therefore is expected to exhibit an extremely low rate under atmospheric process conditions.

When the solids temperature exceeds 800 °C (in a non-catalyzed system) the conventional low rate gasification stage (LRGS) is accelerated and under atmospheric pressure conditions this particular stage can be approximately reduced to the carbon steam reaction with CO and H₂ being the main products which can be combined with certain gas phase reactions under chemical equilibrium conditions. At this temperature level the heavy volatile matter and the fixed carbon content of the solid fuel being processed become reactive. Apart from the char, the tar already released at lower temperatures as well as that being produced in parallel with the gasification reactions participates in an independent reaction rate scheme from that of the solid char. This hypothesis is in accord with the experimental observation of measuring lower tar concentrations at the exit stream of gasifiers operating at high temperatures [3].

The rotary kiln gasifier mathematical model simulates a steady-state gasifier operation and encompasses mass and enthalpy balances over a differential control volume. The formulation of the model resulted in a mathematical system composed of *fourteen differential equations* with an equal number of independent functions (axial distributions of different magnitudes). The remaining axial distributions and final values of magnitudes are deduced from the above-mentioned independent functions. Comparisons of model predictions with the pertinent experimental data will be discussed in following sections of this work.

Experimental

The allothermal rotary kiln chemical reactor type has been or is being tested as a candidate gasifier via the operation of the following two pilot plants.

Pilot plant A (about 100 kg/h raw solid fuel)

The first pilot plant A owned by the Public Power Corporation (PPC) of Greece was designed, constructed and operated in the context of a project funded jointly by PPC and NATO-SFS and directed by one of the authors (G. P. A.). The main research results

obtained by operating this plant were published in citation [7]. A brief account of the process equipment is provided here below, and a flow sheet is shown in fig. 2.

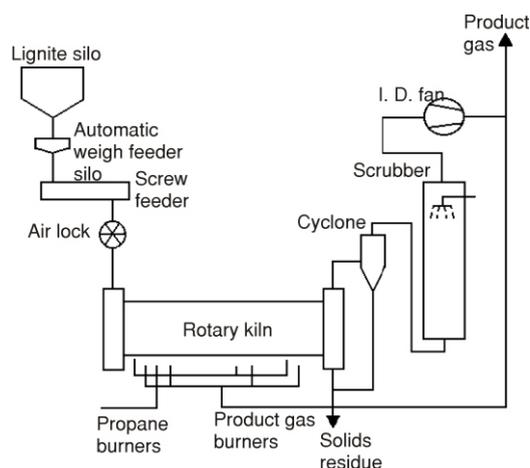


Figure 2. Pilot plant A basic flow sheet

The main equipment was a 6 m long and 0.4 m wide indirect heat rotary kiln made of a heat resistant alloy (incoloy 800 HT). Propane was used as an auxiliary fuel for start up heating purposes. However industrial gasification plants should employ cheaper though clean fuels (*e. g.*, stored clean gas or good quality liquid fuels) to enable heating during start up. Provisions were made for the burning of recycled product gas. Greek lignite of both Megalopolis (Peloponnese) and Ptolemais (Northern Greece) origin were gasified. The feed moisture content was 40-55% and the particle size $d_p < 15$ mm.

The maximum reaction temperature was varied over the range 700-900 °C and the pressure was nearly atmospheric. Solids residence time was varied between 40-80 min., referred to the total kiln length, whereas those in the hot reaction zone are estimated to be about 13-25 min. A typical gasification run was implemented in five days continuous operation and demonstrated a *DAF lignite conversion over 90% and an elemental carbon conversion ~80%*. Typical gas product composition obtained from the pilot plant under consideration (ALKIGAS) is presented in tab. 1 and are compared to those valid for conventional gasifiers [7, 17, 22, 25]. Details on the generated results from the experimental project implemented on pilot plant A are referenced in [7].

Pilot plant B (about 10 kg/h raw solid fuel)

The present work reports experimental results on the gasification of Greek lignite by means of the pilot plant B and their comparison with relevant predictions derived

from a theoretical model based on the particular reactor-gasifier configuration and the intended operation conditions. The aim is to validate a DAF lignite gasification scheme, gas product composition and overall heat transfer coefficient correlation under specified gasifier operating conditions.

The basic flow sheet of the pilot plant B is illustrated in fig. 3. The unit is installed in the semi-industrial Laboratory of the School of Chemical Engineering (NTUA) and its design, construction and operation was the responsibility of one of the authors (K. S. H.) [11].

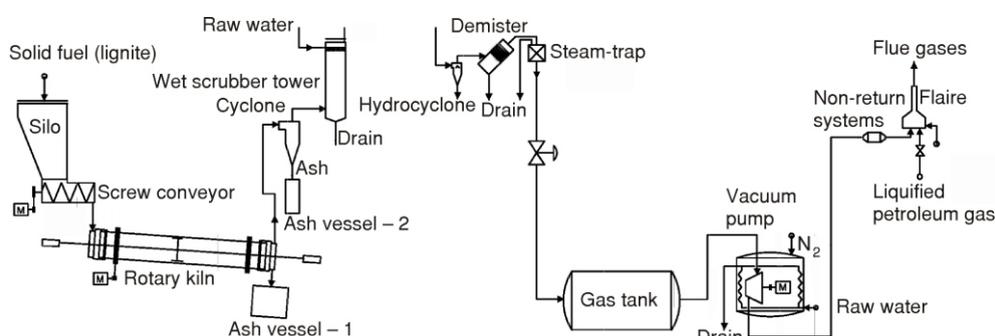


Figure 3. Basic flow sheet of pilot plant B

This pilot plant includes an electrically (indirect) heated rotary kiln reactor (3 m long, 0.12 m wide, heat resistant tube – 316 SS), either bearing or not lifting flights and operating under atmospheric pressure. The reactor is connected to a PLC controller and a PC for data acquisition and control [12].

The pilot unit also includes a gas handling and cleaning (GHC) section. Gas cooling, condensation of the excess steam and heavy hydrocarbons-tar byproducts and the entrained particulates separation are the main functions of the GHC. The operating pressure and the flow rate are regulated through a PID controlled pneumatic valve. The controller is properly calibrated through an algorithm that has been developed for the specific non-linear control system [26, 27].

Pilot plant B is proved to be a flexible to operate pilot gasification installation exhibiting effective phase mixing and enhanced heat transfer. The gasification installation was utilized in a number of research projects as follows. Study of lignite motion pattern through the kiln. The obtained results were reported in [19, 20]. Validation of lignite drying kinetics and overall heat transfer coefficient correlations. The relevant results were published in [12]. Lignite chemical conversion by heating up to temperatures in the range 600-900 °C (Pyrolysis of dried lignite occurs in an inert atmosphere. Indeed, the indirect heat rotary kiln reactor provides for an operation under a controlled atmosphere), *Gasification of raw lignite at temperature 600-900 °C* [11]. Steam is generated *in situ* by

evaporating the lignite inherent moisture content. We recently installed a steam generator which offers the possibility of varying the feed moisture content to the desired level exceeding that of the inherent moisture percentage that the lignite feed carries with it. Also a separate unit of solids feeding was constructed to enable sorbent feeding independently from the fuel feeding stream.

Results and discussion

Experimental results from pilot plant B

The gasification plant was used in the following studies [11]: (1) solids motion through the rotary kiln via the execution of residence time distribution (RTD) measurements, (2) drying, pyrolysis and gasification (max operating temperature 679-880 °C) to investigate the production of clean *synthesis gas*. Additionally several technical studies were conducted aimed at the design, installation and operation of various devices and minor pieces of equipment connected to the main pilot installation for an improved plant operability and automation. To this end details are provided in [11].

During the operation of the flighted rotary kiln under ambient conditions, the tracer pulse stimulus and response technique was applied to study the motion of solids through the kiln and the relevant RTD data were collected [19, 20]. Emphasis was placed in assessing the impact that the lifting flights shape (*i. e.* rectangular, that for an equal horizontal or equal angular distribution of cascading solids) and the rate of kiln rotation impart on the shape characteristics of the RTD and the corresponding mean residence time. The effect of the rate of drum revolution and the drum slope on the non-flighted (bare) kiln operation was also investigated.

Moreover we carried out a study of the drying process of Greek lignite (Megalopolis origin) both experimentally by operating the kiln as an *allothermal* dryer and theoretically by developing a process simulation. The theoretical model apart from the relevant steady-state mass and energy balances employs an empirical correlation for the kinetics of Megalopolis lignite drying [12, 28].

In addition to that we performed experimental gasification runs using partially pre-dried Greek lignite (Megalopolis) as feedstock, under the following operating conditions: (1) solids feed: 5 kg/h, particle size +2 –5 mm and initial moisture content ~30%, (2) Kiln operation data: max internal temperature in reaction zone 670-880 °C, rate of kiln rotation $\omega = 3.85$ rpm, estimated residence time for the entire kiln length ~60 min. (about 20 min. in the hot reaction zone), run duration: ~24 hours. In tab. 2 proximate analysis data are given for the lignite feed been used in the gasification tests. It is to be noted that moisture content of the feed (about 30%) was well below that of the raw material of about 60% *as received basis*. A summary of the gasification results are provided in tab. 3.

Briefly, the following results were obtained from the study of the Greek lignite pyrolysis and gasification processes. The rotary kiln reactor gasified quite effectively moist (30% and over) raw lignite feeds made up of a mixture of coarse-pulverized mate-

Table 2. Proximate analysis data of the lignite gasification feed [11]

Maximum kiln internal temperature [°C]	Moisture [% w/w]	Volatiles [% w/w]	Ash [% w/w]	Fixed carbon [% w/w]
671	33.7	16.3	34.1	15.9
700	33.7	16.3	34.1	15.9
877	20.0	30.0	34.1	15.9

Table 3. Results from gasification runs in pilot plant B [11]

Maximum kiln internal temperature [°C]	Conversion [%]			Gas composition [% v/v]						LHV [MJ/Nm ³]
	DAF* lignite	Volatile matter	Fix carbon	H ₂	CO	CH ₄	CO ₂	N ₂	Tars**	
671	–	–	–	35.8	28.4	4.4	18.6	12.8	–	9.0
700	44.7	83.4	5.2	38.1	24.2	2.9	15.0	19.8	115	8.2

* DAF = dry ash free

** As total dissolved elemental carbon (total carbon – TC), in mg/L, in the wet scrubber effluent stream

rial (*i. e.* –5 mm) and produce a medium heating value gas. This is an advantage accruing from the application of an allothermal mode of operation whereas the production of hot combustion gases to meet the process heating requirements is not done *in situ*. Thus the combustion air being used instead of oxygen is not allowed to dilute the gasification mixture. Moreover the pilot plant enabled the quantitative identification of various operation data the most significant being the fuel conversion, the effectiveness of phases mixing and the overall heat transfer coefficients.

The operation of rotary kiln gasifier (pilot plant B) in daylong, continuous flow, steady-state gasification runs reached DAF lignite conversions up to 80%. The experimental program where the rotary kiln was used, had several targets, the most important being: (1) to assess the impact of the kiln internal architecture on the solids mean residence time and hold-up, as well as the rate of heat exchange, (2) to study the lignite allothermal drying, intended for the production of steam free of combustion gases, and (3) to validate the theoretical model concerning the design and allothermal operation of the rotary kiln for intended applications as solids fuel dryer, pyrolyzer, gasifier, each one at a time or all three in a single unit.

Pyrolysis of lignite in pilot plant A (PPC) [7] resulted in the production of a better quality gas, but lower DAF lignite conversion, in comparison to those obtained under gasification conditions (tab. 4).

Operation of the pilot plant B at low gasification temperature (*i. e.* hydro-pyrolysis experiment) resulted in the production of inferior quality gas and DAF lignite conversion than those measured under gasification conditions (tab. 4).

Table 4. Comparison of performance data for gasification pilot plants A and B

	DAF lignite conversion	Gas product heating value
<i>Plant A (PPC gasifier)</i>		
Pyrolysis of dry lignite	~ 50%	11.7-17.2
Gasification of moist lignite	>90%	10.3-13.8
<i>Plant B (NTUA gasifier)</i>		
Lignite hydro-pyrolysis	~ 45%	8.2-9.0
Gasification of moist lignite	~ 80%	10.0

Operation of the pilot plant B at low gasification temperature (*i. e.* hydro-pyrolysis experiment) resulted in the production of inferior quality gas and DAF lignite conversion than those measured under gasification conditions (tab. 4).

The synthesis gas yielded in allothermal kiln gasifiers (PPC and NTUA) is equivalent to that produced either in a pressurized allothermal fluidized bed gasifier or in conventional autothermal gasifiers under severe operating conditions, strict feed specifications and being run with oxygen as oxidizing medium. The research results on Greek lignite chemical conversion confirm the view that lignite is a highly reactive low heating value fuel. This is usually attributed to its pore structure characteristics which favor heterogeneous reactions [29, 30]. Moreover the enhanced lignite reactivity is also due to the catalytic effect exhibiting by alkaline ash constituents [31]. These facts explain the quite satisfactory performance of the rotary kiln as gasification reactor.

The pilot plant data can be fully utilized in scale up studies aimed at the development of a design for an industrial allothermal gasification plant appropriate for the processing of low heating value solid fuels and the production of a clean gas to fuel an IGCC electric power generating system. However, the thermal efficiency should be the objective for further investigations at a bigger scale (*i. e.* demonstration plant) and be improved further through the use of proper techniques for heat integration.

Greek lignite is a characteristic fossil fuel of low heating value, which can be satisfactorily gasified under mild conditions of pressure and moderately high temperature conditions with the use of an allothermal gasifier.

Comparison of gasification data with theory

Theoretical model predictions are generally in good agreement with the relevant experimental data. The theoretical interpretation indicates that the gaseous phase species at the reactor exit conditions are approaching chemical equilibrium, but a similar situation cannot be verified from the model for the gas-solid reactions (*i. e.* that occurring on the active sites of char). Therefore the need for further laboratory scale lignite kinetic investigation is imperative.

In more detail, the predictions of the theoretical model were compared with the corresponding experimental data yielded from the allothermal rotary kiln gasifier and the

result is depicted in fig. 4. The data shown in figs. 4a and 4b come from a gasification test at maximum internal kiln temperature of 700 °C. This test is in fact a lignite hydro-gasification experiment. In figs. 4c and 4d results are illustrated that were obtained from a gasification run performed at maximum gasification temperature of 877 °C. This is obviously a combined lignite hydro-pyrolysis and gasification experiment. The plots of figs. 4a and 4c demonstrate the consistence between the predicted axial temperature distributions and those measured experimentally. The latter represent the prevailing average temperature at the specified axial kiln positions during the steady-state kiln operation.

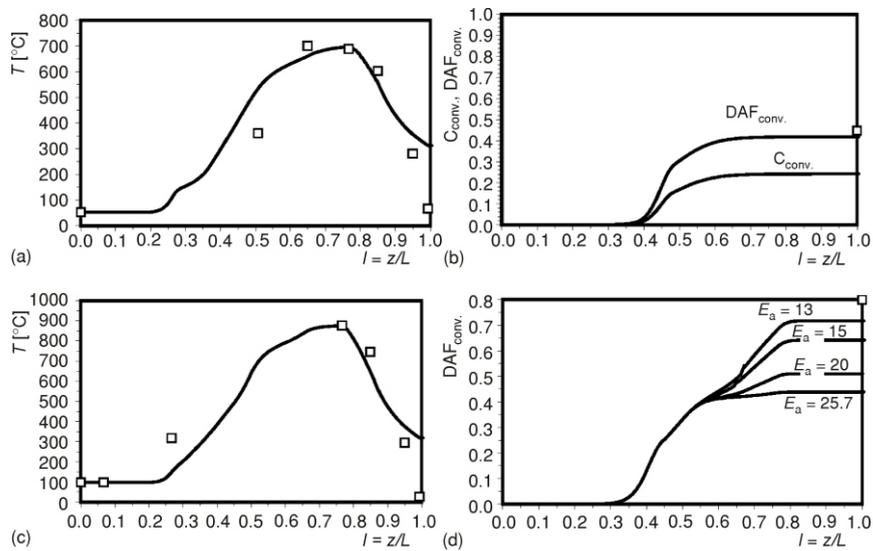


Figure 4. Comparison of experimental with theoretical temperature profiles along the kiln axis – (a) and (c). DAF coal conversion vs. kiln length – (b) and (d). Maximum internal temperature 700 °C (a) and (b) and 877 °C (c) and (d); $L = 3$ m

The distribution of DAF and elemental carbon conversion along the kiln length are plotted in figs. 4b and 4d. For the hydro-pyrolysis experiment we observed a quite successful agreement between the predicted and the measured DAF lignite conversion values at the kiln exit (*i. e.* one can notice at the far right end of the DAF line of fig. 4b the close approach of the curve with the measured DAF value being indicated with an open rectangle). Nevertheless, the prediction of the elemental carbon conversion is appreciably lower than that of the DAF conversion. This can be attributed to the fact that during the pyrolysis process the DAF lignite conversion is associated with an extensive release of elemental oxygen to form other oxygen containing gaseous chemical species.

Regarding the experiment of the combined hydro-pyrolysis and gasification, the predicted DAF lignite conversion values deviate substantially from the corresponding experimental data when use is made of the activation energy of $E_a = 25,2$ kcal/gmol proposed by Johnson [3]. On the contrary the use of a much lower value of about 13 kcal/gmol cited in [32] moves the DAF conversion line upwards and quite close to the relevant experimental point (open rectangle of fig. 4d).

To the extent the investigation proceeded in the present work for each one of the cases being examined the theoretical model predicts with sufficiently good accuracy the product gas composition and heating value. The graphs of fig. 5 represent the predicted variation of gas composition along the kiln length whereas tab. 5 tabulates numerically

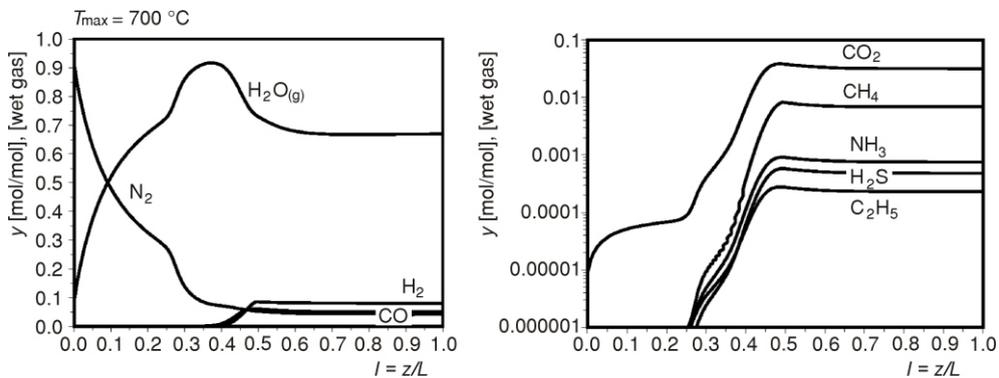


Figure 5. Prediction of gas composition distribution along the kiln axis. Typical lignite hydro-pyrolysis test at 700 °C (relevant numerical values in tab. 5) (the right hand side plot a magnification of the gas components profiles appearing in the lower right corner of the left plot)

Table 5. Comparison between experimental and predicted dry gas composition at the rotary kiln exit; $T_{max} = 700$ °C

Composition of dry gas [% mol/mol]	Measurement	Prediction
H ₂	38.1	37.4
N ₂	19.8	20.3
CO	24.2	23.7
CH ₄	2.9	3.2
CO ₂	15.0	14.7
NH ₃ ⁽¹⁾	–	0.4
H ₂ S ⁽²⁾	–	0.2
C ₂ H ₆ ⁽³⁾	–	0.1

- (1) Gas nitrogenous substances expressed as equivalent
- (2) Gas sulfurous substances expressed as equivalent
- (3) Gas hydrocarbons with C₂ expressed as equivalent

both experimental and theoretical product gas composition data at the reactor exit. The data of tab. 5 for the characteristic hydro-pyrolysis run (*i. e.* at 700 °C) provide a good evidence for the consistency between theoretical and experimentally measured dry gas composition at the gasifier exit.

Hydrogen enriched synthesis gas production

We are presently working on the gasification of lignite-lime mixtures. The scope is to investigate the effect of a sorbent (lime) and process operating conditions (*e. g.*, gasification temperature, particle size, solids residence time and mixing conditions, *etc.*) on the composition and the production rate of a synthesis gas enriched in hydrogen by diminishing the carbon oxides, tars, H₂S content. The addition of lime is intended for drawing the water gas shift reaction towards the production of H₂ by decomposing water at the expense of CO.

The pilot plant B gasification research facility is being employed to carry out this research task. Steady-state continuous flow gasification runs are being carried out using raw Greek lignite (Amynteo, northern Greece) either with or without mixing a sorbent (Greek lime from Koropi of Attica, Greece). In several gasification runs mixtures of raw lignite/lime = 1/2 (mass fraction) with particle size in the feed of +2 –5 mm were processed. Steady-state gasification tests demonstrated the production of gas possessing a high (*i. e.* 70-80% v/v) H₂ and reduced amounts of CO, CO₂ (*i. e.* about 10% v/v). It is to be noted that gasification of the same lignite feed without mixing it with lime produced a gas containing 40-50% H₂, 25-29% of CO, 26-28% CO₂, and 3-4% CH₄ (N₂ free basis). The latter results concern operation at two discrete temperature levels *i. e.* $T_{\text{mean}} = 720\text{-}750\text{ }^{\circ}\text{C}$ and $T_{\text{mean}} = 810\text{-}820\text{ }^{\circ}\text{C}$. Gasification over $T_{\text{mean}} > 800\text{ }^{\circ}\text{C}$ favors high DAF lignite conversions but the CO content tends to increase. Similar gasification test on biomass-lime mixtures strongly indicate the production of synthesis gas enriched in hydrogen (~ 60% v/v in the dry gas) albeit the tar content represents about 50% of the converted DAF biomass matter. However the work is in progress and it is premature to draw firm conclusions on various aspects of the process under investigation.

Conclusions

The rotary kiln reactor technology offers a promising alternative for the chemical conversion of solid fuels into a clean gas proposed for diverse applications. Presently, a high priority is the production of hydrogen, a clean fuel, to be used in electric energy generation and the CO₂ capture. The indirect heat rotary kiln gasifier can be employed in a single stage process for the simultaneous drying-pyrolysis-gasification of solid fuel feeds and the production of a medium heating value synthesis gas, free of air and combustion products admixtures. However the alternative of selecting a sequence of three separate process stages is feasible and has to be decided in energy and environmental protec-

tion efficiency and profitability terms. The results reported herein demonstrate the gasification of raw lignite (high moisture and ash percentages, feed with wide particle size). Furthermore, despite the use of air as oxidizing medium, the allothermal kiln gas possesses a composition and heating value comparable to that produced by the oxygen blown conventional gasifiers. The gasification kinetic modeling is not an easy task due to the complexity of the individual process steps, the big number of parameters to be controlled and experimentally validated. Due to the appreciable residence time of solids and the gas in the kiln a thermodynamic equilibrium analysis should not be overlooked. If chemical equilibrium will be confirmed then the gas product composition and chemical equilibrium conversion can be readily predicted. To this end, further coal conversion kinetic and thermodynamic studies are required since the theory being used in this work showed a good but partial success and therefore needs to be further tested and improved.

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