GASIFIER TO CONVERT NITROGEN WASTE ORGANICS AT SEAL SANDS, UK

Introduction

With respect to thermodynamics it makes no principle difference whether conventional fuels, industrial residues, household or commercial wastes are gasified. Consequently, companies all over the world as well as Noell Technologies GmbH are using their experience gathered in coal gasification in order not only to dispose of residual and waste materials, but to utilise them to a very large extend for chemical productions and to cover energy demands.

The technical philosophy followed by Noell is to convert residual and waste materials in strict compliance with environmental standards and using various modifications of an entrained-flow gasification technology into a raw synthesis gas which can further be utilised in resource and energy recovery.

To cover a wide-ranging menu of fuels, residual and waste materials of different consistency, lumpiness, ash content, chemical composition or calorific value, and to meet the requirements of such in part extremely divergent characteristics, several types of gasification reactors have been developed, a survey of which is given in Fig. 1.

Noell's many years proven standard entrained-flow gasifier of the cooling screen-design is suitable for the gasification of any ash-containing and homogeneous feed materials including pneumatically conveyable solid feeds such as pulverised coal or coke, as well as pumpable feed materials such as oils, tars, sludge and the like.

Heterogeneous feeds such as household waste or its fractions, sorting residues and other lumpy materials cannot be supplied in this form into the entrained-flow gasifier, but need intense pre-treatment. This problem, however, can be resolved by a combination of pyrolysis and gasification.

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For ash-free or low-ash feed materials such as fuel oils, synthesis residuals or hydrocarbon-containing gases a completely or partly refractory brick-lined reactor with cooling wall is used. The technical solution developed for the gasification of black liquor, a spent liquor from the KRAFT pulping process of wood, is also based on the cooling screen principle. For protection against the attack of the highly aggressive liquid salt smelt, a ceramic inliner of high chemical resistance is applied to a special-design cooling screen.

**Reactor Designs**

The basic version of the Noell entrained-flow gasifier originates from the GSP process which was developed by Deutsches Brennstoffinstitut Freiberg for the gasification of pulverised brown coal. The reactants which are fed in at gasifier top (Fig. 2) are converted in a flame reaction. The oxygen-to-fuel ratio is trimmed to keep the gasification temperature at a level at which the inorganic matter melts, flows vertically downward in parallel with the gasification gas and leaves the gasifier through a special discharge unit. With that, carbon conversion rates of more than 99% are achieved. Dependent on the further use of the gas produced, a direct-contact water spray quench system or an indirect-cooling heat recovery steam generator system may be installed downstream of the gasifier. The gasification chamber is enclosed by a cooling screen (Fig. 3) which consists of a gas-tight membrane wall structure that is studded and refractory-lined with a thin layer of a special SiC ramming mass for protection. The liquid slag which is thrown from the gasification chamber onto this cooling screen cools down and solidifies, thus, forming a compact slag layer. This solidified slag layer continues to grow in thickness until the ash fusion temperatures are exceeded. Slag then hitting the wall remains in liquid condition, flows downward the wall and discharges at the bottom together with the gasification gas. Such type of gasifier has successfully been operating at SVZ Schwarze Pumpe since 1984, first on brown coal and then on sludge, ash-containing oils and slurries.

The reactor design with cooling screen requires gasification feeds with ash contents of more than 1% by weight allowing the solidified slag layer to regenerate continually. This is not given, if the ash content is lower. In this case a cooling wall reactor design (Fig. 2) is used, where a refractory lining takes the place of the missing slag layer. A water cooling jacket is substituted for the tube screen inside the pressure vessel. The gasification gas outlet zone, where small ash
quantities may concentrate, is designed as a discharge unit of the cooling-screen type. Low ash quantities enable partial quenching to temperatures of 800 °C, for example, with heat recovery steam generation at higher pressure levels.

In Table 1 potential feed streams and process objectives of Noell’s gasification technologies are summarised.

**Utilisation of Nitrogen Waste Organics**

In various caprolactam and acrylonitrile production processes (Fig. 4 and 5, respectively) considerable amounts of production residues are generated that include mixtures of nitriles, amines as well as cyanide and ammonia compounds. So far these waste fuels were incinerated, but the high NO\textsubscript{X} concentrations in boiler flue gases, in particular, entail high costs or environmental pollution.

A most attractive technical solution shall be demonstrated by example of the gasification facility under construction at BASF plc. The nylon synthesis processes operated by BASF plc. at its Seal Sands site near Middlesbrough, UK, generate in various stages about 110,000 tonnes per year of production residues, part of which is currently disposed of by incineration. Said production residues are liquid, low-ash mixtures of different substances mainly comprised of nitriles, amines and ammonium sulphate that can be assigned to 4 groups of substances, the ultimate analyses of which are shown in Table 2. In future, these compounds which contain up to 24 % by weight of organic-bond nitrogen shall be gasified and, thus, converted into a synthesis gas to drive a gas turbine for the time being.

Before commencing the development of a respective technology, the degradability of organic nitrile and amino groups as well as the hydrogenation of sulphates into sulphides had to be verified. In particular, it was necessary to answer the principle question whether the primary form of nitrogen bond does or does not affect the HCN/NH\textsubscript{3} content of gasification products. For resolution of this question, in addition to thermodynamic calculations gasification trials were run in a test facility of Noell in Freiberg (Fig. 6, 7). Due to their high nitrile and amine contents substances under Group 1 were chosen for the tests (Tab. 3). The tests were run at a
throughput capacity of 150 kg/h, a process pressure of 20 bar and a gasification temperature of 1350 °C. The gasification test results according to Figure 8 show substantially higher concentrations of HCN and NH$_3$ as against the values indicated by thermal equilibrium of approximately 60 mg/Nm$^3$ and approximately 20 mg/Nm$^3$ for NH$_3$ and HCN, respectively. The HCN concentration is, thus, 30 times the value calculated by equilibrium, the NH$_3$ concentration 20 times. This effect, however, is typical for gasification, and is not to be attributed to the nitrile or amino groups.

For comparison, the figures determined in sewage sludge as well as hard and brown coal gasification showing similar deviations are specified in Table 4. The ranges given for hard and brown coals encompass the results of a multitude of tests.

Considering this experience, the test results demonstrated that organic nitrogen compounds such as nitrile and amine mixtures are degradable to elemental nitrogen by gasification under reducing conditions, which meant that no fundamentally different problems were to be expected as already known from gasification technology in general, i.e. the prerequisites for engineering a commercial-scale plant were given.

**The Seal Sands Gasification Island**

Based on the aforesaid gasification test results, the decision was taken by BASF plc. Seal Sands to award Noell-KRC Energie-und Umwelttechnik GmbH a contract for a facility for the gasification of the nitrogen waste organics specified in Figure 9, with following requirements to be fulfilled with respect to the cleaned product gas:

- particulates content $< 10$ mg/Nm$^3$
- sulphur (H$_2$S, COS) content $< 25$ mg/Nm$^3$
- nitrogen (NH$_3$, HCN) content $< 20$ mg/Nm$^3$
- export pressure $\geq 25$ bar

Certain requirements in relation to the overall technology, and to the supply of gasification feeds, the design of the gasification nozzle and the control and safety-related monitoring of the system,
in particular, resulted from the fact that the four feed streams to be gasified are not miscible, with feed rates varying between zero and full capacity. The design of the gasification nozzle is based on the pressure atomisation principle. Due to the high moisture content of feed streams 3 and 4, in particular, the supply of steam as atomisation and gasification medium was intentionally omitted to avoid unnecessary effluent loading of the process. Due to the very low ash contents of feed materials a reactor design with cooling wall according to Fig. 2 was used with the reaction chamber being enclosed by a high-alumina refractory lining. In consideration of the experience gained in the aforementioned gasification tests the design was based on an equilibrium temperature of 1400 °C which entails an oxygen requirement of 4,500 Nm³/h.

Owing to the very low ash content, a water-spray partial quench configuration can be used to cool down the raw gas, once it has left the gasification chamber, from 1400 °C to 800 °C, and a downstream HP steam generator can be installed to recover the sensible heat of the raw gas.

A hot gas filter upstream of the COS/HCN hydrolysis reactor shall protect the catalyst bed of the latter from dust settlement. In the hydrolysis stage that is operated at temperatures of between 220 °C and 240 °C the COS content is reduced by 95 %, and the HCN content is completely eliminated. Following LP steam generation and cooling, where ammonia is removed together with the large condensate quantities, the pre-cleaned raw gas enters the desulphurisation unit. To simplify matters with respect to the relatively low sulphur output of 100 to 150 kg/h, the SulFerox process was chosen for direct oxidation of hydrogen sulphide to elemental sulphur. The clean gas output of approx. 14,500 Nm³/h is then available at a pressure of 26 bar for the specified use, for the present to drive a gas turbine.

The facility under construction has been completed in September of this year. Subsequently, the off-line and on-line functional tests will be performed within another six months.

(In the course of the lecture pictures of the gasification facility under construction will be shown).
Figures

Fig. 1 Noell Entrained-Flow Gasification
Fig. 2 Noell Entrained-Flow Gasifiers
Fig. 3 Reactor Cooling Screen
Fig. 4 Routes for Caprolactam Production
Fig. 5 Typical Acrylonitrile Process
Fig. 6 Gasification Facilities of Noell Technologies GmbH in Freiberg
Fig. 7 Schematic Flow Diagram of the Test Facility
Fig. 8 Equilibrium Concentrations of HCN and NH$_3$ (related to dry raw gas) in the System C, CO, CO$_2$, CH$_4$, CHO, CN, C$_2$N$_2$, H, H$_2$, H$_2$O, HCN, N, N$_2$, NH$_3$, N$_2$H$_4$, NO$_x$, O$_2$
Fig. 9 Generalised System Schematic of the Seal Sands Gasification Island

Tables

Tab. 1 Feed Streams and Process Objectives of Noell’s Gasification Technologies
Tab. 2 Seal Sands Feed Analyses
Tab. 3 Chemical Composition and Calorific Value of Test Material
Tab. 4 Composition of Gasification Gases