

Methanol Synthesis with Steel Mill Gases: Performance Investigations in an On-Site Technical Center

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An on-site laboratory with direct access to cleaned and conditioned steel mill gases was recently put into operation. The long-term performance and stability of Clariant's MegaMax[®]800 methanol synthesis catalyst utilizing steel mill gases is currently being investigated. First test results revealed that in order to investigate deactivation mechanisms arising from particular properties of the cleaned steel mill gases, the overlaying effect of thermal deactivation of the catalyst has to be minimized.

Keywords: Carbon2Chem[®], Catalyst testing, Methanol synthesis, Steel-mill gases

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1 Introduction

Methanol is an important platform chemical for the chemical industry and a promising alternative fuel for combustion engines. The methanol production has steadily increased in the past decades to around 110 million metric tons in 2018 [1]. The feedstock for methanol synthesis is mainly based on fossil raw materials, i.e., natural gas and coal, worldwide [2]. To establish new, sustainable production routes for methanol, the joint project Carbon2Chem[®] is investigating the use of carbon-containing steel mill gases for methanol production. The successful technical implementation of such a process would not only reduce the CO₂ footprint of the steel mill, but also explore a new carbon source for the chemical industry within a cross-industry network.

In the currently ongoing second project phase of Carbon2Chem[®], Clariant's industrial methanol synthesis catalyst MegaMax[®]800 is being investigated using real steel mill gases. Fraunhofer UMSICHT operates a laboratory setup in the Carbon2Chem[®] technical center at the thyssenkrupp Steel Europe site in Duisburg, Germany. The technical center was established in the first project phase of Carbon2Chem[®] and is located close to the steel mill for direct utilization of the most important steel mill gas streams: blast furnace gas (BFG), basic oxygen furnace gas (BOFG), and coke oven gas (COG). Their compositions are shown in Tab. 1.

Fig. 1 shows the technical center including steel mill gases supply, process unit for gas cleaning, and conditioning and lab facilities.

The aim of the present work is to present first results of the MegaMax[®]800 catalyst regarding long-term perfor-

Table 1. Main components of steel mill gases in mol % [3].

| Component | Coke oven gas | Basic oxygen furnace gas | Blast furnace gas |
|-----------------|---------------|--------------------------|-------------------|
| H ₂ | 63 | 5 | 4 |
| CO | 7 | 64 | 25 |
| CO ₂ | 2 | 17 | 23 |
| CH ₄ | 22 | 0 | 0 |
| N ₂ | 6 | 14 | 48 |

mance and stability, taking into account the availability and composition of steel mill gases, which are changing depending on steel production. Additionally, these gases partly exhibit high CO₂ concentrations and a significant share of N₂, which acts as an inert compound in the methanol synthesis process (compare Tab. 1).

One focus of the experimental work is the investigation of synthesis gas streams based on BFG and BOFG and their effects on the MegaMax[®]800 catalyst since fluctuations in

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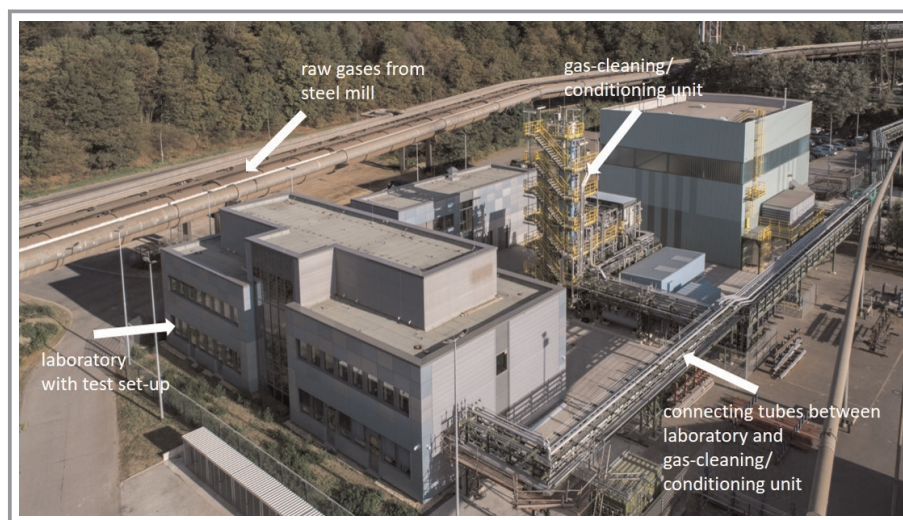


Figure 1. View on the Carbon2Chem[®] technical center at thyssenkrupp Steel Europe site in Duisburg, Germany (reproduced and modified with permission of thyssenkrupp).

the availability and composition of these syngas streams can have an influence on catalyst performance and the reaction itself.

However, the investigation of fluctuating steel mill gases makes the highest demands on the applied test arrangement and requires sophisticated test operation and evaluation. The laboratory test setup used with its technical features is described in detail in Sect. 3.

A specific composition of the syngas used for catalyst testing has not yet been determined, since at this research stage, various gas utilization and conditioning scenarios for the later technical implementation are considered. At this point, process simulation is a valuable tool for test planning as it helps to identify suitable operating points for catalyst testing with regard to a highly efficient process economy and CO₂ saving potentials for certain gas utilization and conditioning scenarios.

The simulation results are characterized by a huge set of parameters as not only the syngas composition but also the process conditions have to be determined. A limitation to essential driving factors helps to reduce the complexity, so that promising operating points for methanol synthesis are identified, which can then be investigated and validated using the laboratory test setup.

The setup now operated in the technical center was used in the first project phase for intense tests of the MegaMax[®]800 catalyst utilizing synthetic model gases at Fraunhofer UMSICHT in Oberhausen, Germany. The application of the same setup allows a direct comparison of the previous results with the current results under real steel mill gas conditions. Sect. 2 describes in more detail the gas cleaning and conditioning unit at the technical center. After 4 years of practical and theoretical work in the Carbon2Chem[®] project, the task will be now the long-term practical testing with real syngas from the gas cleaning and

conditioning unit. Therefore, reliability of the setup and prior experience are crucial factors for sound test results.

2 Gas Cleaning and Conditioning Unit at the Technical Center

The gas cleaning and conditioning unit (cf. Fig. 2) consists of different sections for removing and/or converting of trace compounds. At the outlet of the gas conditioning unit, different syngas compositions related to the aimed utilization scenarios are available. The gas streams are optionally based on BFG, BOFG, or mixtures of them. A pure

hydrogen stream is generated from COG. The following conditioning unit includes a CO shift unit with a high-temperature (HT) shift reactor and a consecutive low-temperature (LT) shift reactor, followed by a methanization unit, in which traces of CO are converted to methane, and finally, a CO₂ separation unit. The CO/CO₂ ratio can be adjusted in a wide range. The conditioned steel mill gas streams are enriched with hydrogen generated from coke oven gas or from a water electrolyzer. Hence, a huge variety of syngas compositions is available. The generated gases are supplied via a direct line to the laboratory in the technical center, which is operated by Fraunhofer UMSICHT. A flow scheme of the gas cleaning and conditioning unit as well as the gas distribution to the laboratory is shown in Fig. 2.

3 Experimental/Methods

3.1 Laboratory Setup for Methanol Synthesis

The laboratory is connected to the pipe bridge that carries the tubing of the outgoing gas streams of the gas cleaning/conditioning unit (see also Fig. 1). This junction point is approximately 40 m from the outlet of the gas cleaning/conditioning unit. Smaller tubes of an outer diameter of approximately 20 mm branch off this junction point to the laboratories. The pressure of the syngas and the pre-cleaned gas is between 0.7 and 0.8 MPa. The laboratory that is referred to in the following is more than 20 m from this junction point.

For a typical methanol synthesis test, the required gas flow is about 0.3–0.8 L_Nmin⁻¹. Due to the above-mentioned distance between the laboratory and the gas cleaning/conditioning unit, it is necessary to increase the volume flow by a factor of 20–30 to purge the pipes. Otherwise, due to the

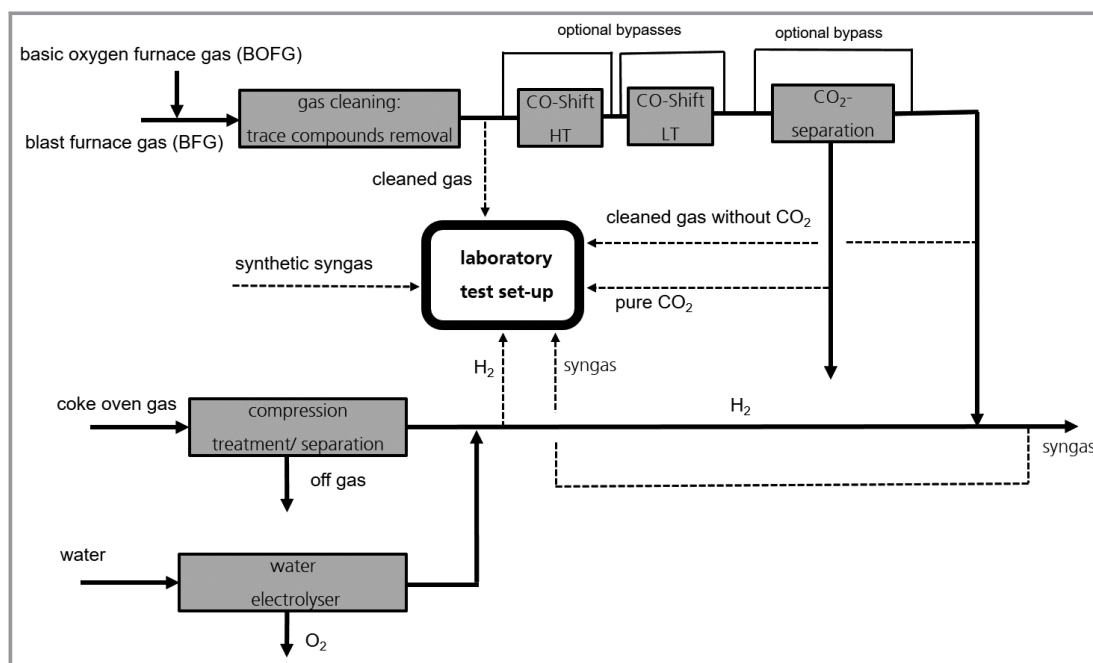


Figure 2. Flow scheme of the different gas streams provided by the gas cleaning and conditioning unit of the technical center to the laboratory for methanol synthesis.

length of the pipelines, a cleaned steel mill gas with the current composition after the gas cleaning/conditioning unit would only be available for the test setup with a significant time delay.

A flow diagram of the test setup including the gas feeding system is given in Fig. 3. When the syngas enters the laboratory fume hood, the gas passes an adjustable overflow valve to generate a sufficient back pressure for the mass flow controllers of the gas feeding system. Behind the valve, the major share of the gas stream is purged to the exhaust gas line. Only a branch stream is fed to the test setup. While the steel mill gases pass the gas cleaning unit, the water concentration increases due to process steps that require additional steam. A gas dryer/cooler at the inlet of the setup reduces the water concentration to a dew point of 276.5 K to prevent uncontrolled condensation in the gas feeding line of the cleaned steel mill gas. A subsequent membrane filter holds back any droplets coming from the condensation.

Complementary to the supply with cleaned and conditioned steel mill gases, the laboratory is fitted with a gas supply of pure laboratory gases, which comprise the main compounds N₂, CO, CO₂, and H₂. With these gases, any desired gas composition is possible. As one of the main tasks of the described work is to evaluate the influence of real gases on the catalyst, a direct comparison to pure synthetic gases is possible.

Pure laboratory gases from a central gas distribution system and the real gases from the gas cleaning unit are dosed to the test setup with mass flow controllers at pressures below 1 MPa. The advantage is that dosing of pure CO₂ is easily possible without condensation issues. The pressure

level of the gas cleaning unit is sufficient for dosing the real gas streams like cleaned BFG or a conditioned syngas. No further pressure elevation is necessary. Thus, the gas supply of the laboratory setup provides a very flexible gas composition of synthetic gases and real gases depending on the aim of the experiment. The gas mixture is subsequently compressed with a piston compressor to working pressure. The compressed syngas is preheated in a reactor tube filled with inert silicon carbide. Thereafter, the gas enters the tubular reactor in which the methanol synthesis takes place. The catalyst is positioned between an upper and lower supporting layer of silicon carbide. Inside the catalyst bed, there are three thermocouples. One is positioned at the inlet of the bed, one at the end, and one in the middle. The reaction temperature is controlled by the thermocouple in the middle of the catalyst bed. The inner diameter of the reactor is 9 mm. Depending on the aimed space velocity, the amount of catalyst varies between 0.5 and 3 g, diluted with silicon carbide. Transport limitation inside the original catalyst tablets might affect the results of the observed reaction rate. To minimize this effect, the original catalyst tablets were crushed and sieved to a smaller particle fraction of 250–500 μm [4–7]. Additionally, the use of this small particle fraction reduced the effect of wall channeling in the fixed bed reactor [8]. The analysis of the feed gas and the composition of the reactor outlet gas stream is carried out with an online gas chromatograph (GC) with thermal conductivity detector (TCD) and flame ionization detector (FID). The tests were performed with the MegaMax[®] 800 methanol synthesis catalyst provided by Clariant. The detailed test conditions can be found in [9].

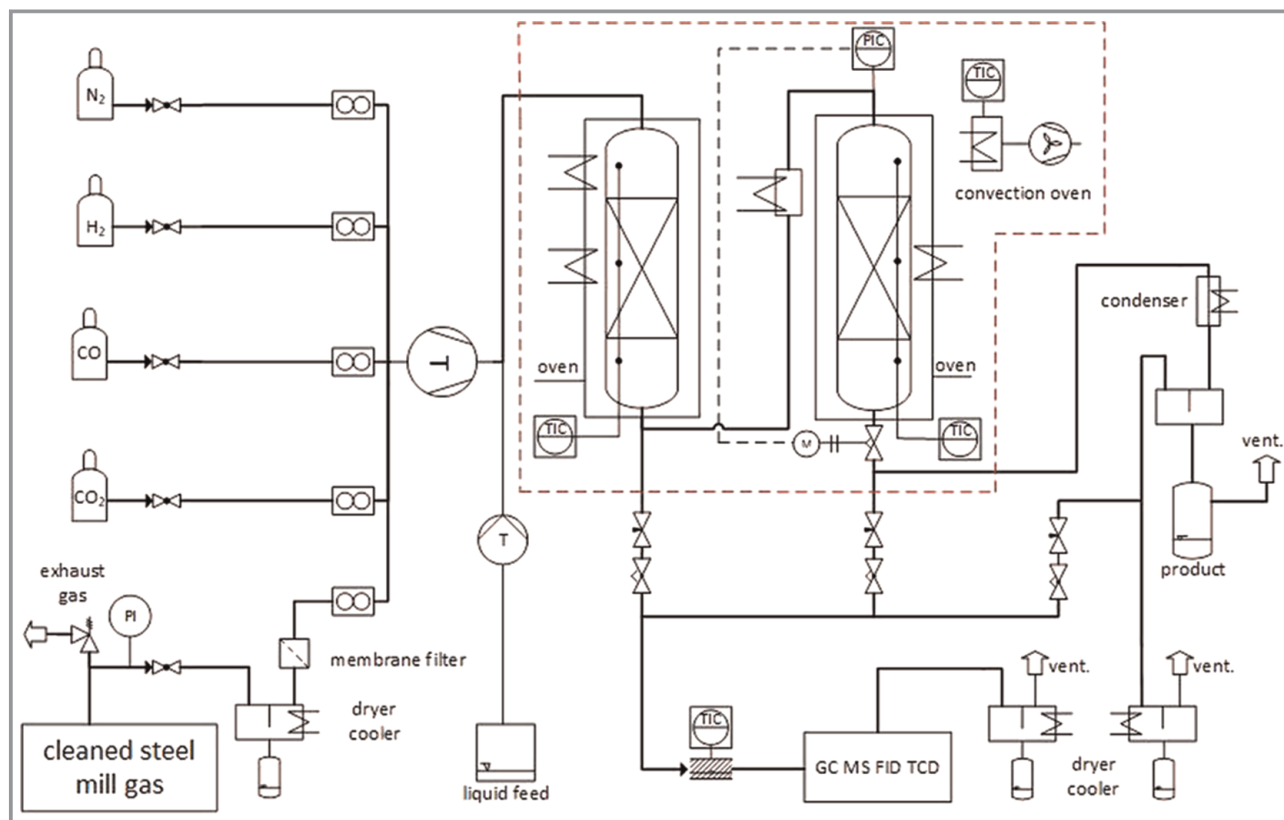


Figure 3. Flow diagram of the laboratory test setup.

4 Results

First, a reference test using a model gas with 73.5% H₂, 13.5% CO, 3.5% CO₂, and 9.5% N₂ was performed to investigate the influence of the activation procedure and the subsequent start-up phase on the methanol catalyst performance. Fig. 4 shows the methanol concentration at the reactor outlet. The methanol formation started while the model gas continuously replaced diluted hydrogen of the activation procedure. Due to a non-disclosure agreement among

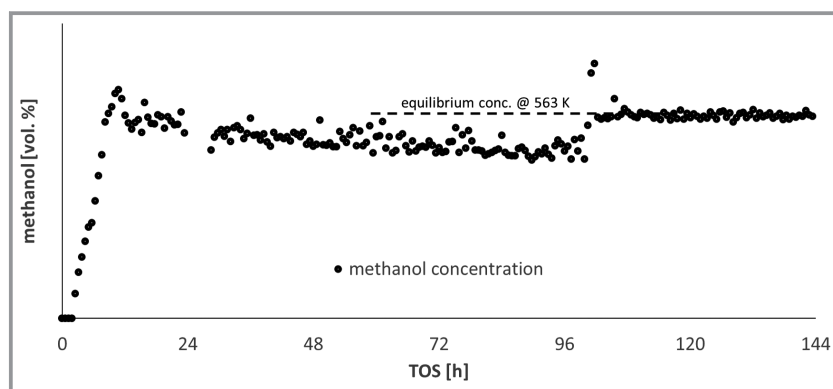


Figure 4. Methanol formation during reference test.

the project partners, explicit methanol concentrations are not shown. The reaction conditions during the first 100 h time on stream (TOS) were chosen to clearly lie in the kinetic regime of the reaction.

It is obvious that after the start-up of the methanol synthesis, the catalyst is highly active but deactivates at 523 K during the first 100 h of the synthesis. This deactivation is mainly caused by thermal deactivation and is usually observed for this kind of catalyst [10,11]. After 100 h, the temperature was increased to an average bed temperature of 563 K. Hereafter, the methanol concentration was nearly constant. An increased methanol concentration occurred due to the elevated reaction temperature. The calculated corresponding methanol equilibrium concentration is marked with a dotted line in Fig. 4. The measured methanol concentrations fit well to this theoretical equilibrium concentration, confirming the accuracy of the setup. In the equilibrium state, no visible deactivation was observed. The performance of the catalyst is consistent with observations made when using technical catalysts for methanol synthesis. After a start-up phase, the state of

the catalyst alters in the syngas stream until the change in the active centers of the catalyst surface is completed by, e.g., deactivation or other processes, and a constant activity is attained [12, 13].

Afterwards, a test series with cleaned BFG was successfully performed to obtain first data and information concerning catalyst performance and stability under realistic reaction conditions. The activation procedure and synthesis conditions in terms of temperature and space velocity were similar to the above-described reference test. The reaction conditions were chosen to provide testing in the kinetic regime. Apart from that, the test was conducted with an elevated pressure of 8.4 MPa to approach conditions closer to the technical process. Finally, prior to the test setup, the cleaned BFG gas was enriched with synthetic H_2 to a stoichiometric value of 2.4. Therefore, the final feed gas consisted of 10.3 vol % CO, 9.5 vol % CO_2 , 56.8 vol % H_2 , and 23.4 vol % N_2 .

The test was run for a total period of 20 days with H_2 -enriched BFG. Before and in between the test series, reference tests were conducted. The methanol formation during the test period and the conducted reference tests are presented in Fig. 5 as normalized methanol concentrations. The time on stream was set to zero when the real gas was introduced. An interruption of the test was necessary after 10 days due to maintenance work at the gas cleaning unit. Within the first 10 days of test operation, a continuous trend of decreasing methanol formation, after a very high activity just after the introduction of the real gas, was observed. A continuous decreasing methanol formation within the first days after start-up of a test was expected and has already been observed in the scope of the reference test with model gas (see Fig. 3). However, it is still unknown if the deactivation trend will continue, potentially due to a cumulative poisoning of the catalyst or other, up to now, unknown effects. Subsequently, the test was continued for

additional 10 days. Deactivation decreased and the activity of the catalyst appeared to be stable. However, to prove whether deactivation really stopped or gradually progresses, further investigation of the long-term stability of the catalyst will be continued.

An important task of the current research is to reveal effects arising from currently unknown trace compounds in the cleaned steel mill gases streams. Hence, the authors suggest a strategy consisting of two laboratory test series. A similar strategy was applied in [14] to investigate the influence of altering CO_2 concentrations on the stability of the catalyst. The first test series starts with a reference gas composition similar to the syngas generated from steel mill gases, consisting of pure synthetic gases. After that, the test is continued with the real syngas after the gas cleaning/conditioning unit for several days up to several weeks, followed by a switch back to the reference gas composition. This part of the test series has to be conducted with the same catalyst sample. Subsequently, for the second part of the test series, a fresh catalyst sample is used. Again, the test has to be performed under the same reaction conditions and with pure laboratory gases exhibiting the same gas composition compared to the real syngas with regard to the main compounds H_2 , CO, CO_2 , and N_2 . Therefore, the exact composition of the real syngas must be known. Now, it is possible to compare the results of the two test series. If significant deviations between the first and the second part of the test series occur, the catalyst might be affected by the composition of the real syngas, arising from trace compounds or other effects that are currently unknown.

5 Conclusions and Outlook

Direct access to cleaned steel mill gases is crucial for a realistic assessment of the performance and lifetime of the

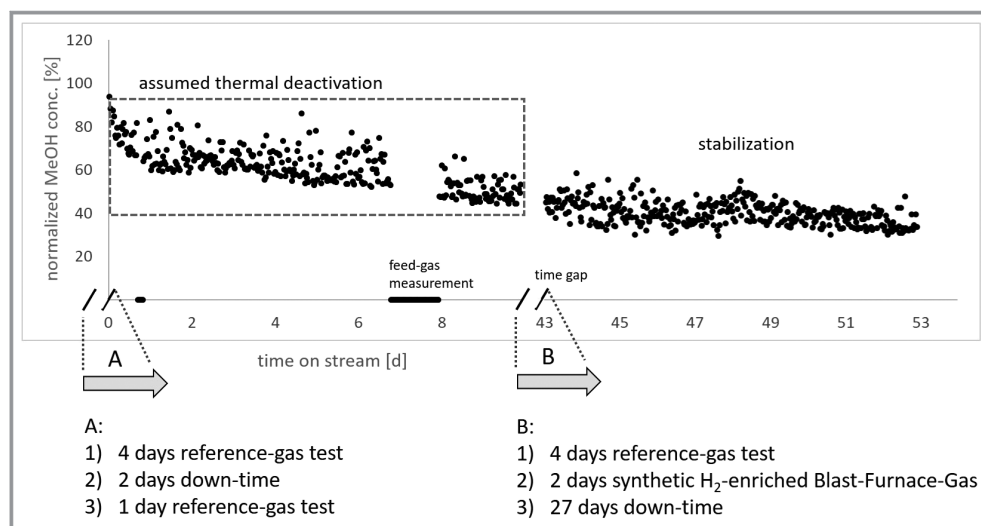


Figure 5. Methanol formation during real-gas test.

industrial methanol synthesis catalyst. A comparison between real gases and synthetic steel mill gases could reveal the effect of trace compounds that could slip through the gas cleaning unit. However, the evaluation of the obtained data is challenging because the effect is overlaid by significant thermal deactivation at least during the first weeks. Up to now, the precise duration of the thermal deactivation period using real syngas cannot be revealed, as only few data exist. Additionally, fluctuating raw gas composition, residence time effects caused by the gas cleaning process, and the gas distribution complicate the identification of correlations. Long-term tests with real syngas, and subsequently, well-chosen reference tests with model gas are required for a reliable prediction of catalyst stability and performance. Recently, a first test, with real H₂-enriched BFG was conducted successfully for a period of 20 days.

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Abbreviations

| | |
|------|-------------------------------|
| BFG | blast furnace gas |
| BOFG | basic oxygen furnace gas |
| COG | coke oven gas |
| FID | flame ionization detector |
| GC | gas chromatograph |
| HT | high-temperature |
| LT | low-temperature |
| TCD | thermal conductivity detector |
| TOS | time on stream |

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