Article Safety Evaluation of Catalytic Synthesis Off-Gases through Explosion Pressure Determination

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Abstract: In this research evaluation, the catalytic synthesis off-gas was investigated through a safety assessment approach. Though operation safety measures are of utmost importance in the industrial processes, they are difficult to maintain when variable components are dealt with. Four different scenarios based on various process phases and off-gas compositions were experimentally evaluated. The results exhibited significant differences in explosion pressure values, revealing the most severe consequences during the start-up phase, when H₂ is abundant, and during the advanced process (over 30 h of operation), when CO is abundant in the off-gas composition. The first case possessed 200 MPa/s explosion pressure change, while the latter was equal to 152 MPa/s. These findings have provided a significant guideline for progressive industrial applications with complex material mass balance.

Keywords: catalytic synthesis; off-gas; explosion pressure; explosion autoclave; safety assessment

1. Introduction

With mounting energy and material demands, increased production capacities and new facilities are being brought into operation. However, with increased technological performance, there is also an increased risk of accidents related to toxic, flammable or explosive materials. The latter bears the hazard of immediate destruction and threat to human life. For these reasons, certified investigations are by law applied upon materials utilised.

The industrial applications with energy gases, such as natural gas [1], syngas [2], hydrogen [3] or mine gas [4], go necessarily hand in hand with the determination of safety assessment associated to the potential explosion [5]. The explosion pressure in various concentrations with ambient atmosphere are usually determined, while explosion characteristics are investigated [6]. The process of catalytic synthesis is not an exception [7]. This process is widely used to convert synthetic gas into various products, such as alternative diesel [8], ammonia [9], ethanol wax [10], chemicals [11] and much more. In some cases, CO_2 instead of syngas might be used in order to reduce the carbon footprint of the facility and enhance its market profit through the introduction of additional products [12]. However, the commercialisation of such an approach is in an early stage, and thorough research must yet be performed on this matter, as well as on conventional H₂/CO catalytic conversion processes.

Studies on the explosion of process gas mixtures have been previously published [13], related to hybrid gaseous/solid mixtures [6,14]. However, every process is a unique configuration of segments and processed substances. In catalytic synthesis, gas composition fluctuates as a function of the exposition-dependant character of the gas-to-liquid (GtL) conversion [15]. As a result, there is no universal explosion assessment applicable across the range of processes as the safety investigation of every individual is essential [16] applied to various phases of the GtL catalysis [17]. In the Fischer-Tropsch GtL process, H₂ and CO gases are usually introduced into the technology at the volumetric rate of 2:1. Due to the explosive nature of H₂ and CO [18], this mixture represents a chief danger, considering the potential power of the explosion. The gas further undergoes numerous chemical reactions [19] on the catalyst surface and degrades in terms of explosivity concentration range, forming CH₄, C_nH_m (up to C₅H₁₂) and CO₂. The final composition of the produced off-gas changes with the used catalyst, operation parameters and also during the process duration itself, as the product character tends to be strongly time-dependent



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before the stabilised regime is achieved [20,21]. As the time-on-stream (TOS) parameter evolves, the selectivity of both gaseous and liquid products undergoes variations. Consequently, the safety assessment must comply with various scenarios, which are susceptible to various technological risks.

Although research studies on explosion pressure assessment of FTS off-gas are infrequent, there are predominant research experiments on other industrial gases. For instance, Inaba et al. [22] studied the explosion characteristics of natural gas and methane utilised for hydrogen production. Application in the semi-open space allowed the authors to predict the influence of the explosion accident. Also, Han et al. [23] focused their study on hydrogen in a premixed gas with air in rectangular channels. The authors observed that the detonation overpressure exceeded the prediction for a hydrogen concentration range of 25 $%_{vol.}$ -45 $%_{vol.}$, while the highest measured pressure was equal to 2899 kPa at 35 $%_{vol.}$. LPG/air mixtures were experimentally studied by Zhao et al. [24], who investigated the suppression effect of the prevalent CO₂ gas in the blend.

Additional studies were carried out on widely used methane blended with air or another single gas compound. However, the catalytic synthesis process usually generated a gas blend of more than six compounds, while the explosion predictive models can only be performed with satisfying precision with up to three gaseous compounds. Such studies on relevant real gases from the catalytic synthesis technologies are missing.

In this study, the catalytic synthesis off-gas was studied through explosion pressure assessment in its different forms during the technology operation. The unique findings represent a basement for further investigation and an important point of view, which was until now not adequately discussed and experimentally evaluated in the research literature. The observation underlines the necessity of precise safety assessment considering variable operation threads in a dynamic system.

2. Materials and Methods

2.1. Catalytic Synthesis Setup and Operation Parameters

The examined off-gases were generated from a catalytic synthesis unit with a fixed bed tubular reactor, operating at maximum temperature and pressure equal to 550 °C and 7.0 MPa, respectively. The reactor volume was 9.4 cm² (8 mm inner diameter). The technology possessed four separate gas inlet valves (flow regulators) calibrated for N₂, H₂, CO and CH₄. The produced liquid/waxy substances were sampled in two branches with different ambient temperatures (120 °C and 30 °C), while the remaining, uncondensed off-gas was passed through a pressure regulator into the flowmeter Definer 220 (MesaLabs, Lakewood, CO, USA). The produced gas was further analysed in Gas 3000p (Pollutek Gas Analysis, Lubbeek, Belgium) molecular analyser, in which the volumetric fraction of H₂, CO, CO₂, CH₄, N₂, C_nH_m and O₂ were determined within a full scale 0–100 %_{vol.}, except for C_nH_m and O₂, where the scale was 0–25 %_{vol.} and 0–10 %_{vol.}, respectively.

The catalytic substance based on active Co was selected in this study. This catalyst was developed on an Al_2O_3 support of spherical particles of 1 mm diameter and was promoted with Mn (3.8 %_{wt.}) and K (0.9 %_{wt.}), while the content of active Co was equal to 14.0 %_{wt.} for better selectivity towards desired liquid products.

More information about the catalytic synthesis setup and the used catalyst is available at Čespiva et al. 2024 [25]. The detailed breakdown of operation parameters is seen in Table 1.

Parameter	Unit	Value	
Temperature	[°C]	280/310	
Pressure	[MPa]	1.5	
GHSV	$[h^{-1}]$	1145	
GHSV/C	$[1 \cdot g^{-1} \cdot h^{-1}]$	1.4	
Catalyst mass	[g]	8	
Inert SiO ₂ mass	[g]	2	
H ₂ activation temperature	[°C]	400	
H ₂ activation pressure	[MPa]	0.1	
H ₂ activation duration	[h]	4	
H ₂ gas flow	$[1 \cdot h^{-1}]$	4.5	
CO gas flow	$[\mathbf{l} \cdot \mathbf{h}^{-1}]$	5	
CH ₄ gas flow	$[1 \cdot h^{-1}]$	2	

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2.2. Explosion Autoclave for Pressure Determination

The source gases, the off-gas from the catalytic synthesis process, were delivered in 50 L Tedlar bags immediately after the volumetric flow and molecular composition determination. The investigation of safety and

explosion parameters was carried out using experiments on a circular stainless-steel double-walled explosion autoclave 497-OZM-15 (OZM Research, s.r.o., Hrochův Týnec, Czech Republic). The constant volume of this device was 0.02 m^3 . The apparatus consists of an explosion chamber, a temperature control unit, a spark generator (burner), a vacuum pump and a data acquisition system. A digital temperature controller A 30 (JULABO, GmbH, Seelbach, Germany) was used to set the temperature for heating and cooling the apparatus using an oil circuit. The temperature control system was employed to set the temperature in the range of 20–60 °C with a temperature fluctuation of less than 2 °C. The initial temperature in the autoclave was measured by calibrated thermocouples with an accuracy of 0.5 °C, located in the upper part of the chamber. An electrical discharge initiated the gas mixture in the chamber at 15 kV and 20 mA with a delay time of 85 ms. The electrodes were positioned in the middle of the explosion chamber with a spacing of 5 mm. The dynamic explosion pressure was recorded by a pair of piezoelectric silicon pressure sensors. A schematic diagram of the explosion autoclave technology is presented in Figure 1.



Figure 1. Explosion autoclave of 0.02 m³ volume.

3. Results and Discussions

3.1. Off-Gas Quality and Quantity

Based on the above-described procedure, four different off-gases relevant to four different stages of the catalytic synthesis were investigated through a safety assessment approach. The gas composition labelled as A represented the state when synthesis was not operational (no reactions take place). Such a scenario might occur when technology undergoes a sudden shutdown using a bypass for the introduced input gas. It is also a composition relevant to the input gas itself, where only H_2 and CO are present. Scenario A can be marked as the most explosive and threatening one from the safety point of view.

Once the catalytic reactions occurred, the input gas was consumed and transformed into desirable liquid products. The off-gas which consisted of gaseous products, mostly CH_4 and CO_2 , while lighter C_nH_m occurred, as seen in scenario B (5 h of TOS), as presented in Figure 2. The C_nH_m value was mostly represented by ethane, while compounds up to butane were present in small amounts.

After an initial 5–10 h of operation, the strong reaction activity phase changed its course towards increased production of liquid hydrocarbons at the expense of process wastewater. In this phase, the amount of produced off-gas increased, from approx. 5 to 6 l/h. Unreacted CO and H₂ were present in the gas again (scenario C at 15 h of TOS). With advanced TOS, the stabilised regime experienced a change in the composition of the product. This phenomenon might be due to changes in catalyst activity, degradation, and shift of the dynamic temperature field [26]. The occurrence of unreacted CO and H₂ further increased at the expense of other remaining gaseous products (scenario D in 30 h of TOS). The composition of the off-gas in the steady operation state is quite in line with other studies on catalytic synthesis with Co catalyst utilised, and can be considered usual [27,28].



Figure 2. Evolution of the catalytic synthesis off-gas composition; (A) before synthesis (0 h), (B) active start-up period (5 h), (C) stabile operation regime (15 h), (D) advanced stabile operation regime (30 h).

3.2. Explosion Parameters of the Off-Gas

The graphs in Figures 3–6 present the explosion curve, built upon individual explosion pressure determination experiments in various real off-gas/air blends. From the graphs, it is obvious that in scenario A (Figure 3), the explosive range was the broadest, stretching from 5 $\%_{vol.}$ to nearly 80 $\%_{vol.}$ of the off-gas/air concentration.



Figure 3. Explosion pressure of various off-gas/air concentrations (scenario A, 0 h).



Figure 4. Explosion pressure of various off-gas/air concentrations (scenario B, 5 h).



Figure 5. Explosion pressure of various off-gas/air concentrations (scenario C, 15 h).



Figure 6. Explosion pressure of various off-gas/air concentrations (scenario D, 30 h).

This occurrence might be due to H₂, the explosion concentration of which was 4–75 $%_{vol.}$ A similar statement applied to pressure change dp/dt, with a maximum value, i.e., 200 MPa/s at 42 $%_{vol.}$ concentration, was the uppermost achieved in this study. However, the maximum pressure p_ex equal to 0.9 MPa at 35 $%_{vol.}$ concentration did not significantly exceed other findings in this study.

In scenario B (Figure 4), when catalytic synthesis was strongly active during the first operation hours, the measured explosion pressure reached 0.7 MPa at 17 $\%_{vol.}$ concentration, and the same value was attended during the stabilised operation regime (scenario C presented in Figure 5). This comparison is in line with findings presented in Figure 2, where it is evident that there is only little difference in the synthesis process going between 5 h and 15 h TOS period. These values are significantly lower than in A scenario, which is generally considered the most explosive and dangerous one, however, the exposition of this gas composition is much longer, offering the longer period of time for potential leakages and unsafe situations.

A noteworthy difference was observed with the advancing process stage (30 h), when the reactions and the product character had stabilised. In scenario D (Figure 6), the maximum explosion pressure value was equal to 0.83 MPa, again, at the concentration of 17 $\%_{vol.}$ Correspondingly, the pressure change measured was much higher (152 MPa/s) compared to scenarios B and C (19 MPa/s and 17 MPa/s, respectively).

This behaviour can be associated to the increased concentration of CO in the off-gas, the content of which amplified more than thrice, from 1.3 $%_{vol.}$ (B) and 4.0 $%_{vol.}$ (C) to 20.4 $%_{vol.}$ (D). Luo et al. [29] reported a substantial finding with applied CO in the CH₄/air blend. Analogously, Deng et al. [30] performed an experiment on CO influence on CH₄ explosion in a 20-L near-spherical autoclave. They found that the explosive limits narrowed, but the maximum explosion pressure improved (up to 0.798 MPa).

All these judgements underline the necessity of a precise safety assessment dependent on exact technological scenarios, unusual process situations, various outputs, etc. Simplified safety assumptions on explosion risk, generated from the predicted or measured gas compounds' concentrations, are not satisfying and real-time experiments must be performed.

4. Conclusions

In this research endeavour, the safety assessment through explosion pressure determination was applied to the catalytic synthesis off-gas. Four different process stages with various off-gas molecular composition were investigated and experimentally evaluated in an explosion autoclave.

Significant differences were notified in the explosion pressure as well as in pressure change parameter as the off-gas underwent a drastic change in composition along the process evolution. The most explosive and, thus, dangerous scenario was determined at the beginning of the process or during the shut-down phase when most of the H₂/CO input gas remained unreacted. The explosive concentration range stretched from 5 %_{vol}. to nearly 80 %_{vol}, while maximum explosion pressure was 0.9 MPa at 35 %_{vol} and pressure change was 200 MPa/s at 42 %_{vol}. Other scenarios were prevalent when H₂ and CO content was diminished at the expense of less explosive compounds. The narrowed explosive concentration range was a consequence of limited H₂ content, however, when the synthesis process stabilised, an increased concentration of unreacted CO reoccurred, which thereby influenced the explosion pressure change, which was measured to be 152 MPa/s at CO = 20.4 %_{vol}.

These significant research outcomes have highlighted that during the catalytic synthesis process, it is crucially important to consider different process phases as they are interconnected to different outputs and materials which are further associated with stringent safety measures. Further futuristic research studies should focus on additional experimental evaluations of these gases as the mathematical models are insufficient in predicting the behaviour of gases that are composed numerous components.

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