

SAFE STARTUP AND SHUTDOWN PRACTICES FOR STEAM REFORMERS

AIGA 086/14

Based on CGA H-11-2013 First Edition

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	Contents	Page
1	Introduction and purpose	1
2	Scope	2
3	Definitions	2
4	General considerations 4.1 Personnel safety 4.2 Emergency response 4.3 Process safety 4.4 Communication 4.5 Recommended operating procedures 4.6 Materials and Equipment 4.7 On-line furnace inspections	
5	Startup	
6	Shutdown 6.1 General shutdown preparation 6.2 Controlled shutdown procedures (planned shutdown) 6.3 Unplanned shutdown 6.4 Isolation and purging of flammable gas systems in preparation for maintenance.	15 15 17
7	Training and procedures	18
8	References	10

1 Introduction and purpose

1.1 Introduction

As a part of a programme of harmonization of industry standards, the Asia Industrial Gases Association (AIGA) has adopted the Compressed Gas Association (CGA) standard H-11.

This international harmonized document is intended for use and application by all IHC member associations. The AIGA edition has the same technical content as the CGA edition, however, there are editorial changes primarily in formatting, units used and spelling. Also, references to regional regulatory requirements have replaced US regulations where appropriate.

Large scale hydrogen production has been commercially practiced for decades and the demand for such production has grown over that period. In the last several years, developments in crude oil processing, such as the increased use of hydrogen to remove sulfur and the refinement of heavier crude oil stocks, has driven significant growth in the demand for hydrogen supply.

In response to this demand, industrial gas companies operate and maintain large scale hydrogen production facilities worldwide and have done so with an exemplary safety record for many years. However, it should be noted that large scale hydrogen production involves potential personnel and process safety hazards that must be addressed in design and operation. Such hazard potential is inherent to the processing of toxic and flammable gases via high temperature reforming as practiced in hydrogen production.

The steam reformer represents the core operating unit of most large scale hydrogen production facilities. Therefore, steam reformer furnace combustion safety is fundamental to the overall safe operation of these large scale hydrogen plants. The startup and shutdown of the reformer can create transitional periods of increased risk to the operation of the facility. The operating procedures and practices employed during startup and shutdown must effectively address the potential hazards of such transitions to ensure plant safety.

The need to specifically consider and address the startup and shutdown of industrial processes is well recognized as a cornerstone to safe operation. Requirements to ensure startup and shutdown safety are addressed in operating procedures and are included in process safety regulations in Title 29 of the U.S. Code of Federal Regulations (29 CFR) Part 1910.119, *Process safety management of highly hazardous chemicals*, referred to as OSHA Process Safety Management (PSM), and in Europe, Directive 96/82/EC *on the control of majoraccident hazards* (known as the Seveso II Directive), among other regulatory bodies [1, 2].

Guidelines for the safe startup and shutdown of industrial production units are technology specific. Industry-wide publications addressing startup and shutdown practices exist for many technologies, including industry publications such as AIGA 056/08, *Safe Practices Guide for Cryogenic Air Separation Plants*, which addresses startup and shutdown of air separation plants [3]. At this time, no such industry-wide guidelines have been compiled and published for steam reformer operation.

It should be noted that there are other industries, such as ammonia and methanol production, that operate large steam reformers. Therefore, it may be instructive to consider the learning and experiences from those industries through organizations such as the American Institute of Chemical Engineering: Ammonia Plant Safety Symposium and the International Methanol Producers and Consumers Association (IMPCA).

Steam reformer furnace design will continue to develop along with methods to implement combustion safety in these furnaces. A wide variety of steam reformer designs, configurations, and component equipment exists today. Therefore, this publication includes generalized statements and recommendations on matters which there may be diversity of opinion or practice. Users of this publication should recognize that it is presented with the understanding that it can supplement, but not take the place of, sound engineering judgment, training, and experience. It does not constitute, and should not be construed to be, a code or rules or regulations.

1.2 Purpose

The purpose of this publication is to inform and guide interested parties on the procedures and practices fundamental to combustion safety in the operation of steam reformers. This publication presents a baseline for safe reformer operation which, if followed, assures our customers that the hydrogen they receive from member

PAGE 2 AIGA 086/14

companies has been produced according to accepted industry-wide safety guidelines. This publication provides a technical basis that can be used to present a common viewpoint to government and regulatory authorities, ensuring proper application of rules and regulations.

2 Scope

This publication applies to steam reformers that are operated with natural gas, refinery off gas, naphtha, and other light hydrocarbon streams. It specifically applies to large volume hydrogen production plants, defined for this publication as a production capacity of 380 000 scfh (10 000 Nm³h) (9 MMSCFD or 240 000 Nm³D) or greater. This publication may be applied to smaller reformers depending on the technology used.

This publication covers operational safety of steam reformer startup and shutdown. Emphasis is placed on operational guidance and features that provide safeguards against the hazards associated with the transition and infrequent nature of startups and shutdowns. The publication is not intended to address the details of design, installation, construction, and initial startup (commissioning) of steam reformers.

3 Definitions

For the purpose of this publication, the following definitions apply.

3.1 Publication terminology

3.1.1 Shall

Indicates that the procedure is mandatory. It is used wherever the criterion for conformance to specific recommendations allows no deviation.

3.1.2 Should

Indicates that a procedure is recommended.

3.1.3 May

Indicates that the procedure is optional.

3.1.4 Can

Indicates a possibility or ability.

3.2 Boiler

Closed vessel in which water is heated and steam is generated by heat input from combustible fuels in a self-contained or attached furnace.

3.3 Burner

Device for the introduction of fuel and air into a combustion chamber at the velocity, turbulence, and concentration required to maintain ignition and combustion of fuel.

3.4 Burner management system (BMS)

Control system dedicated to combustion safety and operator assistance in the starting and stopping of fuel preparation and combustion equipment and for preventing improper operation of and damage to fuel preparation and burning equipment.

3.5 Bypass

Means used to temporarily deactivate an alarm, control, or protection system including, but not limited to: jumper wires, control system overrides, forced values, modified set-points, modification of the normal lock open or closed valve positions, taking the device off-line, or running temporary hoses. Based on the type of bypass, it can also be referred to as an override, shunt, or jumper.

3.6 Bypass log

Formal document used to track the approval, installation, management, and removal of bypasses.

3.7 Cold collector

Refractory lined piping system wherein the exit of the catalyst tubes are directly connected to a refractory lined piping manifold.

3.8 Combustion air

Air used to react with the fuel in the combustion process.

3.9 Convection section

Portion of the reformer, downstream of the furnace, where flue gas passes over heat exchangers and heat transfer occurs via radiation and convection.

3.10 Damper

Valve or plate for controlling draft or the flow of gases, including air.

3.11 Dead leg

Section of a piping system that normally has no significant flow (one end blocked or restricted) with a length greater than 3 to 6 pipe diameters.

3.12 Double block and bleed (DB&B)

Piping or instrument arrangement that combines two block (or isolation) valves in series with a vent valve in between the block valves as a means of releasing pressure between the block valves with the intent to provide positive isolation.

3.13 **Draft**

Negative pressure (vacuum) measured at any point in the furnace, typically expressed in inches of water column (mm of water column).

3.14 Excess oxygen

Flue gas oxygen measurement, typically on a wet gas basis (e.g., 1.5% excess oxygen approximately corresponds to 10% excess air, depending on fuel composition).

3.15 Extended outage

Period of time after a plant shutdown that can range from several weeks to months.

3.16 Forced draft (FD) fan

Device used to pressurize and supply ambient air to the combustion chamber to support combustion.

3.17 Flame

Body or stream of gaseous material involved in the combustion process and emitting radiant energy at specific wavelength bands determined by the combustion chemistry of the fuel. In most cases, some portion of the emitted radiant energy is visible to the human eye.

3.18 Flame detector

Device that senses the presence or absence of flame and provides a usable signal.

3.19 Furnace

Portion of the reformer where the combustion process takes place.

3.20 Header

Pipe or duct through which liquid or gas is conveyed and supplied to or received from multiple branches.

3.21 Induced draft (ID) fan

Device used to remove the products of combustion from the reformer furnace by introducing a negative pressure differential.

3.22 Interlock

Device or an arrangement of devices, in which the operation of one part or one mechanism of the device or arrangement controls the operation of another part of another mechanism.

PAGE 4 AIGA 086/14

3.23 Lower explosive limit (LEL)

Lowest concentration of a flammable gas in an oxidant that will allow a flame to propagate when ignited.

NOTE—LEL is sometimes referred to as lower flammability limit (LFL).

3.24 Lock closed valve

Manual valve that is closed in its safe position during normal operation. The valve is locked in the closed position by means of a plastic strip, a cage around the valve, a key locked chain, or another suitable device.

3.25 Lock out tag out (LOTO)

Safety procedure used to ensure that sources of energy are properly shut off, isolated, and labeled prior to the start of maintenance work. This condition is maintained during the work, and reversed when preparing for restart

3.26 Monitor

To sense and indicate a condition without initiating automatic corrective action.

3 27 Parmissive

Condition that must be met before a piece of equipment can be operated or a step in a sequence can be completed. After the equipment is operated or sequence step is completed the permissive is ignored.

3 28 Prereformer

Reactor, located upstream of the reformer, that primarily converts heavy hydrocarbons (e.g., ethane, propane, butane) to methane.

3.29 Pressure swing adsorption (PSA)

Multiple fixed bed gas purification process that uses materials that selectively adsorb one or more gas species from a mixture. Regeneration of the adsorbent is accomplished with a pressure reduction or swing.

3.30 **Purge**

Flow of air or an inert medium at a rate that will effectively remove any gaseous or suspended combustibles and replace them with the purging medium.

3.31 Pyrophoric

Capable of igniting spontaneously in air.

3.32 Radiant section

Portion of the furnace in which the heat is transferred to the tubes, primarily by radiation.

3.33 Refinery off-gas

Gas stream removed as a by-product or purge from various crude oil processing units; typically consisting of a mixture of hydrogen, olefins, and alkanes.

3.34 Safety instrumented system (SIS)

Independent system composed of sensors, logic solvers, and final elements designed for the purpose of:

automatically taking an industrial process to a safe state when specified conditions are met; and/or

permitting a process to move forward in a safe manner when specified conditions allow (permissive functions).

3.35 Startup

Series of steps to initiate process flows, increase process temperatures, and start production.

3.35.1 Hot restart

Startup occurring shortly after an instantaneous shutdown from a no-hydrocarbon feed flow and near operating temperature condition to an operating flow condition at operating temperature.

3.36 Shutdown

Series of steps to stop production, feed, and fuel flows in a safe and controlled manner.

3.36.1 Planned shutdown

Series of scheduled activities to shut down the process in an organized and well prepared manner. This type of shutdown is usually done in preparation of a planned or extended outage.

3.36.2 Unplanned shutdown

Shutdown initiated by an input to the control system (manual pushbutton) or by a logic action (interlock) within the control system. This type of shutdown is commonly referred to as a trip.

3.37 Steam reformer

Processing unit where steam is reacted with hydrocarbons over a catalyst at high temperatures to produce hydrogen and carbon oxides. The reformer includes a furnace/radiant section and a convection section.

3.38 Steam to carbon ratio

Molar ratio of water to carbon present in the reformer feed as hydrocarbon.

3.39 Tail gas

Low pressure contaminant rich rejection stream from pressure swing adsorption.

3.40 Transfer header

Refractory lined pipe that connects the reformer outlet manifold to the inlet of the waste heat boiler.

4 General considerations

4.1 Personnel safety

All personnel present in the plant (outside the control room or buildings) during startup or shutdown shall wear personal protective equipment (PPE) as required by site policies or regulations. See AIGA 082/13, Combustion Safety for Steam Reformer Operation, and AIGA 066/10, Selection of Personal Protective Equipment for more information [4, 5]. PPE shall adhere to applicable regulatory standards. PPE should include:

- safety glasses with rigid side shields;
- hard hats;
- flame resistant clothing (FRC);
- hearing protection;
- safety shoes;
- gloves; and
- portable personal gas monitors.

All personnel should have proper hazard awareness including familiarity with safety data sheets (SDS) for hydrogen, feedstock, fuel, and other chemicals and catalysts present in the area. All personnel present during startup or shutdown operations shall be trained in accordance with company procedures. See Section 7.

Additional considerations for unit shutdowns:

- Catalysts containing nickel shall not be exposed to gases containing carbon monoxide at temperatures below 390 °F (200 °C) to avoid the formation of nickel carbonyl. During shutdown, the nickel-containing catalyst should be purged with steam or nitrogen gas prior to reaching the nickel carbonyl critical formation temperature. If this does not occur, precautions shall be taken to avoid exposure risk to personnel. Plantspecific procedures shall be developed for the prevention of nickel carbonyl formation in steam reformer shutdowns.
- Some catalysts in the process are pyrophoric (e.g., prereformer, shift reactors); therefore, air exposure shall be avoided. The risk of an exothermic reaction and temperature increase is greatest during a plant shutdown, when plant pressure can be near or at atmospheric pressure. Active temperature monitoring

PAGE 6 AIGA 086/14

should occur during these periods. Plant personnel and contractors shall be knowledgeable of this hazard and shall follow the safety instructions provided by the catalyst vendor.

4.2 Emergency response

Prior to the startup or shutdown of the unit, the following emergency response requirements shall be met:

- availability of site-specific emergency response procedures;
- adequate training of personnel in emergency response procedures;
- availability of firefighting equipment that has been tested and confirmed ready for use (e.g., hydrants, monitors, and extinguishers); and
- availability of communication equipment that has been tested and confirmed ready for use.

4.3 Process safety

For a startup or shutdown, the following process safety factors shall be considered:

- training and competency of plant personnel to perform the startup or shutdown procedures;
- staffing levels adequate to ensure a safe startup or shutdown;
- limiting the number of individuals present in the reformer plant to essential personnel;
- accuracy of startup or shutdown procedures
- compliance with applicable work processes and regulations (e.g., management of change [MOC] and prestartup safety review [PSSR] as per 29 CFR 1910.119 [1]) and
- accuracy of process documentation (e.g., piping and instrumentation diagrams [P and IDs], process flow diagrams)
- effective execution of MOC processes prior to the plant start-up or shutdown.

4.4 Communication

Prior to the startup or shutdown of the unit, the following communication should take place:

- notify customers and/or supplier that the unit will start or stop generating product(s);
- notify utilities that the unit will start or stop drawing utilities;
- notify the appropriate organizations (e.g., local environmental agencies) that the unit will be in startup or shutdown mode;

NOTE—There can be special time limits for completing start up and shutdown and reporting the status in some jurisdictions.

- conduct periodic communication with maintenance personnel to coordinate activities so that the safety of personnel and integrity of equipment is not compromised.
- perform an ongoing review of maintenance activities to ensure they are not jeopardized by the startup or shutdown; and
- notify the organization that the unit will be on startup or shutdown mode, and include confirmation that planning and execution for the unit startup or shutdown has been completed.

4.5 Recommended operating procedures

Site-specific operating procedures should exist to address applicable utility and auxiliary systems, including the following:

process analyzers;

- freeze protection;
- critical local process instrumentation;
- testing and proper operation of safety devices;
- temporary connections management;
- mechanical equipment handling;
- steam and boiler feed water (BFW) systems;
- cooling water system preparation;
- piping and equipment lineup;
- routing of syngas, hydrogen product, and PSA tail gas;
- process piping and vessels purge requirements;
- fuel system preparation;
- ammonia system preparation (if required);
- nitrogen;
- flare or vent system preparation;
- demineralized water supply;
- electric power and uninterruptable power supply (UPS);
- burner management system (BMS) preparation; and
- plant and instrument air.

NOTE—The above list may not be all inclusive due to the individual design of plant equipment.

4.6 Materials and equipment

The following supplies should be available prior to startup and shutdown:

- portable analytical equipment and accessories;
- certified hoses;
- task-specific tools;
- burner ignition equipment;
- safety equipment (e.g., caution tapes and tags, flash lights); and
- breathing air equipment for confined vessel entry.

4.7 On-line furnace inspections

Throughout startup and shutdown periods, frequent visual observations of the furnace interior shall be made through the inspection ports. Special emphasis shall be placed on burner, reformer tube, and reformer refractory inspections as described in AIGA 082/13[4].

PAGE 8 AIGA 086/14

5 Startup

5.1 Pre-startup preparation

5.1.1 General preparation

The following activities shall be completed prior to startup:

 Review the bypass log. All hardwired and software bypasses shall be removed unless authorized under management of change (MOC). During an outage, temporary bypasses can have been used for testing and calibration of mechanical equipment, electrical equipment, and for testing of safety control system actions (interlocks);

- Verify proper BMS functionality prior to start up. The BMS system provides extremely important safe guards during a reformer startup;
- Clear equipment lock out tag out (LOTO);
- Ensure temporary blinds have been removed (per official blind lists) and that lines are properly made up;
 and
- Confirm the position of permanent blinds, spool pieces, and lock open and lock close valves according to the process and instrumentation diagram (P and ID).

Ensure the following utilities and auxiliary services are placed in service:

- normal and emergency lighting;
- nitrogen;
- fuel:
- flare or vent system;
- demineralized water supply;
- steam headers (including steam traps) and condensate headers;
- electric power and uninterruptable power supply (UPS);
- control system;
- burner management system (BMS);
- plant and instrument air;
- cooling tower fans and pumps, boiler feed water (BFW), steam, and cooling systems chemical injection.

NOTE—Confirm quality against specifications for nitrogen, air, cooling water, and demineralized water.

5.1.2 Preparations after an extended outage

For plants that have undergone an extended outage, special startup precautions should be considered. For example:

- plant critical safety systems can have been affected by extended exposure to environmental elements and therefore testing may be required;
- changes to personnel can have occurred and therefore training may be required; and
- changes to offsite conditions can have occurred and therefore plant operating procedures can need to be revised.

5.1.3 Nitrogen purging and leak testing

Before starting the plant, purge process gas piping and equipment with nitrogen until all oxygen is removed. The oxygen content shall be checked in appropriate locations and shall be below the country-specific thresholds prescribed by governing regulations or agreed to standard (e.g., NFPA 56 (PS), Standard for Fire and Explosion Prevention During Cleaning and Purging of Flammable Gas Piping Systems, in the United States) [6]. Pressure purging is accomplished by bringing the plant up to nitrogen system pressure followed by depressurization. This process is repeated several times until the required oxygen threshold is reached. The pressurization/depressurization flow rate should be controlled to regulate the pressure drop in order to avoid catalyst fluidization or crushing.

During pressure purging, appropriate documents (e.g., piping and instrumentation diagrams) should be used to confirm that all sections of piping in the plant, including dead-legs, have been adequately purged.

The following methods may be used to perform leak testing:

- If any part of the system has been opened during the shutdown, pressurize with nitrogen and apply soapy water to the flange and valve connections. The test fails if there are any signs of bubbles; or
- Pressurize the system with nitrogen (below operating pressure) and trend the pressure for approximately 30 minutes. If the pressure decrease is more than 5%, the test fails.

If any test fails, the startup should not proceed. Repair the leak and repeat the testing until no leaks are detected

5.2 Nitrogen flow and reformer ignition

5.2.1 Starting nitrogen flow

Nitrogen flow shall be established through the reformer process prior to lighting the burners. This step requires the nitrogen system to be connected to the process piping. The nitrogen system shall be protected against reverse flow from the process by plant design and/or operating procedures.

Prior to starting nitrogen flow, the following conditions shall be confirmed:

- isolation of the downstream process units (e.g., carbon dioxide removal systems, coldbox, membranes, pressure swing adsorber [PSA]);
- isolation of the hydrocarbon feed line(s);
- low points are drained; and
- vents and drains are closed.

Nitrogen flow may be achieved by once through flow or by circulation with a compressor. A minimum nitrogen flow shall be maintained to ensure reformer tube integrity once the burners are lit. A flow of 1000 scfh to 2000 scfh (28 Nm³/h) to 57 Nm³/h) per tube is typical; however, furnace design requirements for minimum shall be confirmed and followed. The flow measurement element(s) and transmitter(s) used to measure nitrogen or nitrogen mixed with steam during startup are used to measure process flow during normal operation. The flow measurement calculation constants should be adjusted depending on the type of flow meter used to account for the change in service between startup and normal operation. The pressure and temperature compensation calculation of flow measurement shall be properly configured (e.g., signal range, clamping, equation) to ensure accurate flow measurement during startup conditions.

Nitrogen should be slowly introduced, limiting the process pressure change to typically no more than 15 psi (103 kPa) per minute. Proper nitrogen flow should be established according to site-specific operating procedures. System pressure and flow should be monitored to ensure increase to the desired set point.

5.2.2 Starting fans

Fan(s) should be started using the following steps:

PAGE 10 AIGA 086/14

- a) If required, notify the electric power supplier of the intent to start fan motors;
- b) Confirm the following prior to starting the fan(s):
- Reformer inspection port doors should be set in position as specified in the plant operating procedures.
 Doors may be left open in order to facilitate starting the fan(s). Confirm the correct position of the combustion air valves at the burners as well as the dampers and registers in the air distribution system; and
- Ensure the burner fuel isolation valves are closed;
- c) Start the ID fan as per site-specific operating procedures and/or vendor supplied procedures;
- d) If applicable, start the FD fan as per site-specific operating procedures and/or vendor supplied procedures;

NOTE - If an FD fan exists, the ID fan is started first.

- e) Once the fan(s) have been started and stabilized, adjust the fan control(s) to establish and maintain design furnace draft; and
- f) Adjust the fan control(s) to achieve required furnace air flow.

5.2.3 Reformer fuel gas system preparation

The following process shall be used to prepare the reformer fuel gas system:

- a) confirm the feed system is isolated so that hydrocarbon feed cannot be introduced into the reformer tubes;
- b) perform a leak test as described in AIGA 082/13 to ensure that all valves at the burners are fully closed and not leaking [4]; and
- c) ensure that all permissives and interlocks have been cleared.

5.2.4 Burner ignition

The following process may be used to initiate burner ignition:

- a) Slowly introduce fuel into the burner header;
- b) Adjust the combustion air valve or register of the burner being lit;
- c) Using an acceptable ignition source (e.g., portable electronic igniter, torch), slowly open the burner isolation valve until ignition is achieved. Ensure safety guidelines of ignition devices are followed;
- d) Once the burner(s) are ignited, adjust the combustion air valves and registers as required to adjust the flame pattern;
- e) Monitor the furnace draft and adjust fan controls as needed;
- f) Ignite more burners as required in predetermined sequence and pattern (e.g., crisscross pattern) to assure even furnace heat up. The average heat up rate should be less than 100 °F/hr (56 °C/hr) (heat up rate limit to be confirmed by furnace designer) and measured at the point the flue gas exits the radiant section;
 - If the burner ignition sequence is interrupted due to loss of flame, the procedure shall be restarted as outlined in 5.2.3; and
 - Heat up ramp can be limited by the refractory repair dry out procedure.
- g) Monitor the fuel header pressure and adjust as needed.

5.2.5 Heating the reformer with nitrogen

Process parameters should be monitored as temperatures increase and steam production begins. As the operating temperature increases, monitor equipment for thermal expansion including counter weights or spring hangers, reformer tubes, cold collector, transfer header, and boiler. Nitrogen circulation continues as the re-

former temperature increases and until steam is produced in adequate quantity and quality for introduction into the reformer.

The hydrodesulfurization and prereformer sections are heated up during this period. Hydrodesulfurization catalyst performance typically requires a temperature greater than 600 °F (316 °C).

5.3 Steam generation and introduction

5.3.1 Steam quality

5.3.1.1 Catalyst considerations

The contaminants in steam originate mainly from upstream water treatment. Boiler make-up water quality, boiler feed water quality, and steam drum water chemistry (e.g., conductivity, pH) should be confirmed to be within specified limits. Trace elements found in boiler water (e.g., silica, sulfur, sodium) will act as poisons to the catalyst used in this process. If imported steam is used during startup or shutdown, similar considerations with regard to catalyst contaminants apply.

In the absence of hydrocarbons during steam introduction, the potential for catalyst oxidation exists and should be confirmed with the catalyst supplier. Some catalyst suppliers recommend adding hydrogen to steam to reduce the possibility of oxidation. In these cases, maintenance of a steam/hydrogen ratio of 10/1 in mol/mol is generally recommended; however, the exact ratio requirement should be obtained from the catalyst supplier.

In order to avoid exposing catalysts to steam alone, some of the catalyst beds may be bypassed until feed is introduced. The most common examples include prereformers and medium/low temperature shift reactors.

5.3.1.2 Liquid water carry over/vaporization risk

In general, steam lines shall be drained, heated up, and free of condensate before introducing steam to the process. Pushing condensate into a hot reformer can lead to reformer tube ruptures due to a combination of thermal shock and the sudden expansion of liquid into a large volume of steam.

Condensate will accumulate in the piping from the point steam is introduced into the process and in the downstream exchangers based on the plant layout. The condensation risk level depends on the presence of condensate accumulation points in the piping, as well as the local climate. Draining from every low point location (e.g., feed preheat coil, in front of the shift reactor) and warming process gas lines sufficiently to remove condensate are important requirements during a startup.

5.3.2 Steam introduction to the reformer section

Once lines have been purged of condensate and sufficient steam is available, steam is introduced using the following steps:

- a) Steam should be introduced only after all catalyst bed temperatures are above the condensation point at current system pressure;
- b) Once steam flow is above the minimum flow per tube as specified by furnace design requirements, slowly reduce the flow of nitrogen;
- c) As steam flow is gradually increased, nitrogen flow may be proportionally reduced. Sufficient process pressure should be maintained to drain condensate out of the downstream equipment; and
- d) Shut down the nitrogen recirculation compressor (if it exists) and isolate the nitrogen source according to site-specific operating procedures. The design pressure of the nitrogen circuit is normally lower than the normal operating process pressure. Before increasing the setpoint of the process pressure controller, the connection(s) to the nitrogen header or to the nitrogen loop shall be closed (with double block and bleed setup) to avoid backflow of syngas to the nitrogen header.

At startup, localized overfiring can result in overheating and damage to the reformer tubes. Temperature measurement downstream of the reformer in the process gas line may not be a reliable indication of tube temperatures. Due to low flow on the flue gas side the temperature measurement at the outlet of the radiant section can

PAGE 12 AIGA 086/14

also indicate low. It is critical that tube surface temperature is monitored by direct observation during startup. See AIGA 082/13 for details on various process variables that should be monitored to mitigate this risk [4].

Steam should be introduced gradually. The increased mass flow will transfer heat to the temperature sensors in the process gas line downstream of the reformer and the temperature reading will rise. The steam flow rate established before feed introduction should be clearly stated in the startup procedure based on guidelines from the manufacturer. In general, this is approximately 10% of the plant capacity, or 1500 scfh to 2000 scfh (42 Nm³/hr to 57 Nm³/hr) per tube.

5.3.3 Monitoring downstream equipment

Monitoring the downstream heat exchanger in the convection section and process gas stream is critical during startup. During steam introduction, condensate is generated in the syngas cooling section. Condensate should be drained to the water disposal system or recycled back to the boiler feed water system. During the startup phase the process pressure is significantly lower than normal operating pressure. It may be necessary to increase process pressure in order to drain all condensate and to avoid reaching high levels in the separators.

At this point in the sequence, low boiler feed water requirements can lead to a heat transfer imbalance in the boiler feed water exchangers resulting in water boiling and/or water hammering in the exchangers. Both conditions can lead to mechanical damage. Increasing the blow down rate at the deaerator or steam drum can mitigate these conditions.

5.4 Feed introduction considerations

5.4.1 Temperature to start feed introduction

Hydrocarbon feed should be introduced when the process gas temperature downstream of the reformer is in the approximate range of 1000 °F to 1200 °F (538 °C to 650 °C). If the upper temperature limit is exceeded before introducing feed, there is a risk of overheating the reformer tubes. If feed is introduced below the lower temperature limit, there is a risk of carbon formation on the reformer catalyst. The actual temperature of feed introduction depends on feed stock composition and shall be confirmed with the plant design.

5.4.2 Minimum steam flow

It is recommended that the minimum steam to carbon ratio is greater than 5 to 1 during feed introduction. Steam flow should be confirmed using independent measurements having pressure and temperature compensation. Insufficient steam flow during feed introduction will result in a low steam to carbon ratio and will cause carbon formation on the reformer catalyst. If prolonged, the catalyst can suffer irreversible damage. An interlock to prevent a low steam to carbon ratio should be active from the moment the hydrocarbon feed is introduced.

5.4.3 Feed pre-treatment

When the feed at the battery limit contains sulfur, catalyst damage can occur instantaneously if the feed is directly introduced to the prereformer/reformer catalyst without pre-treatment. Therefore, the hydrodesulfurization (HDS) section shall be commissioned ahead of feed introduction to prereformer/reformer. HDS temperatures shall be high enough to ensure adequate sulfur removal. Hydrogen flow to the HDS should be according to the plant design requirements.

5.4.4 LPG and naphtha plants

For LPG and naphtha plants, care shall be taken to ensure preheating of the process lines in order to avoid feed condensation resulting in carbon formation on the prereformer/reformer catalyst.

5.4.5 Temperature changes resulting from feed introduction

When the hydrocarbon feed is introduced, the process gas temperatures downstream of the reformer will decrease rapidly due to the endothermic reforming reaction. As a result, additional firing is required at the moment of or soon after hydrocarbon feed introduction. The heat duty (firing) increase should be proportional to the feed introduction to avoid an excessive decrease in the process gas temperature.

5.4.6 Firing control

As steam and feed flow rates are increased, additional firing is required to maintain the heat up rate. Air flow should be adjusted to maintain excess oxygen within recommended operating limits. During this period, emphasis shall be placed on burner, reformer tube, and reformer refractory inspections as described in AIGA 082/13[4].

5.4.7 Pressure control

The process vent control valve upstream of the purification section shall be in automatic pressure control. During this phase, the pressure controller setpoint is lower than normal operating pressure to avoid steam condensation in undesired locations (e.g., catalyst beds, boiler). After feed introduction, the process gas pressure controller setpoint is slowly raised to the normal operating pressure.

5.4.8 Prereformer

Some plants have a prereformer upstream of the tubular reformer. The prereformer converts heavy hydrocarbons (e.g., ethane, propane, butane) to methane, and part of methane to hydrogen. The prereformer reactors are adiabatic, and depending upon the feedstock, the overall reaction could be exothermic or endothermic. For example, the reaction will be exothermic while processing naphtha, and endothermic while processing light refinery off-gas or natural gas. These reactors typically operate between 788 °F to 932 °F (420 °C to 500 °C). A nitrogen circulation loop with a heater is sometimes provided to preheat the prereformer.

There is a risk of catalyst and/or catalyst vessel damage at higher temperatures. In the case of heavier aromatic feeds, there is a risk of catalyst damage due to a polymerization reaction at lower temperatures. The prereformer catalyst can also be damaged by excessive steaming or high steam to carbon ratio. The catalyst is easily poisoned by impurities such as sulfur and chlorides. The following precautions should be taken for startup of the prereformer:

- the catalyst bed shall be within the temperature range specified by the catalyst vendor;
- the HDS section should be ready (i.e., at recommended operating conditions) to remove impurities from the hydrocarbon feed stream prior to introducing the feed to the prereformer;
- the downstream reformer should be ready (i.e., at recommended operating conditions) for feed introduction in order to minimize the period of steam-only flow to the prereformer catalyst.
- hydrogen should be added prior to adding steam and according to catalyst vendor recommendations; and
- the bed temperature profile should be carefully monitored during the addition of hydrocarbons.

5.5 Establishment of downstream units

A variety of process units can be downstream of the steam reformer to further process the syngas into products. These downstream units can include the following:

- syngas heated reformer;
- high temperature, medium temperature, and low temperature shift reactors (HTS, MTS, LTS);
- carbon dioxide removal systems (e.g., amine systems);
- pressure swing adsorption (PSA) and vacuum swing adsorption (VSA);
- methanator;
- cryogenic separation (also known as a coldbox) including temperature swing adsorption (TSA); and
- membrane separation.

During startup of the steam reformer and subsequent feeding of syngas to the downstream units, it is important to avoid conditions that could lead to damage of these units as they are brought on-line. Proper purging to remove oxygen from the units, as generally described in 5.1.3, shall be completed before the introduction of syn-

PAGE 14 AIGA 086/14

gas. Damage can result from exceeding design temperature and/or pressure including condensing in equipment not designed for a liquid phase, catalyst deactivation (see 5.3.1.1), adsorbent damage, excessive pressure drop, or reverse flow. A thorough review (e.g., Hazard and Operability [HAZOP] study) shall be completed to determine the potential hazards associated with the steam reformer startup conditions relative to each of the process units located downstream of the reformer.

Key elements of a downstream unit startup strategy shall include operating procedures, training, control system actions, alarms, permissives, and interlocks.

5.6 Introduction of additional fuel streams

In many cases, downstream units will separate syngas into multiple streams and return some of the streams back to the steam reformer as fuel. Typical examples include tail gas from a PSA, off-gas from a carbon monoxide coldbox, and permeate/residue streams from a membrane. Additional fuel streams may also be available from external sources (e.g., refinery fuel gas).

Typical piping configuration for an additional fuel system contains a double block and bleed valve arrangement and flow control components. An automatic leak test method may be included in this configuration. Assure these piping systems are purged below the oxygen threshold before introducing fuel. See 5.1.3.

The introduction of additional fuel streams has an impact on furnace pressure, temperature control, and flue gas oxygen content. Therefore, additional fuel streams shall be stable in pressure, composition (density and heating value), and flow prior to introduction to the reformer. The additional fuel streams from external sources can contain liquids; therefore, proper operation of liquid removal systems is crucial.

Potential variation in heating value due to composition changes is of primary concern when dealing with additional fuel streams. Flame stability can be affected as a result of heating value variation. If composition variation is detected, inspections of the reformer should be performed (see 4.7). Indications of variation include unusual performance of the liquid removal system, variation of flue gas oxygen content, variation of furnace pressure, and variation of furnace temperature.

During the introduction of additional fuel streams, the operator should monitor the response of the control system and reformer flame pattern, and be prepared to respond to variances.

5.7 Plant restart after trip

A plant restart after a trip shall only be performed if the cause of the trip is known and the plant is not damaged. An example of such an event includes a temporary interruption of power.

5.7.1 Safety considerations at restart

5.7.1.1 Potential for explosive atmospheres following trips

It is important that a furnace is adequately purged with air to remove hydrocarbons (e.g., fuel gas) before lighting burners. Most plants will have an automated or semi-automated purging sequence, while some plants may have a manual procedure for purging. In most cases, the gas valves to each burner must be manually closed as part of the restart interlock checks. See AIGA 082/13 for additional information regarding combustion safety considerations [4].

5.7.1.2 Steam drum levels

Control of the steam drum level is important as it provides temperature protection to steam generation equipment. Prior to restart, drum level shall be under control and boiler feed water shall be available.

5.7.2 Hot restart

A hot restart refers to the reintroduction of hydrocarbon feed while reigniting burners shortly after a trip. At this point, the reformer is hot enough to avoid steam condensation in the system. The plant owner should set the criteria for a hot restart on a per plant basis, as condensation can occur in many places depending on the process units in the system. Steam flow through the reformer tubes shall be sufficient for handling the heat input

without overheating the tubes as burners are relit. As burners are reignited, steam flow should immediately increase to the point where hydrocarbon feed may be introduced.

Plants that use a nitrogen recirculation loop should have strict criterion for when a hot restart can occur. Steam shall be available in sufficient quantities to provide cooling. In some plant designs, once through nitrogen flow is used to provide cooling. If conditions are not adequate to produce steam immediately, or there is no back up steam supply available, nitrogen flow is continued until there is sufficient steam flow.

Once appropriate steam flow is achieved and proper temperature conditions are met, startup may continue. See 5.4.

5.7.3 Cold restart

If a hot restart cannot be carried out, use of a cold start procedure is required. See 5.2.

6 Shutdown

6.1 General shutdown preparation

Planned shutdown of a steam reformer will stop production in a manner that is deliberate and executed according to a documented procedure. Key elements of a controlled shutdown that shall be included in such a procedure are outlined in the following sections.

Appropriate notifications should be made to concerned or impacted parties prior to beginning the controlled shutdown. Communication may be directed to facility management, maintenance teams, project organizations, customers, and suppliers.

The following items should be confirmed for planned shutdowns:

- Pre-shutdown maintenance activities will not be impaired by shutdown activities;
- Shutdown work permit system is ready for implementation by trained personnel;
- Nitrogen system is ready for increased use and additional volume needed for shutdown is available;
- Critical manual valves (not routinely used) are ready for operation;
- Temporary piping is installed or is ready for installation (if needed). Confirm that a management of change (MOC) process is followed if an operating procedure is not available;
- Supplies are accessible (e.g., explosimeters, analyzers, draeger tubes, special PPE).

6.2 Controlled shutdown procedures (planned shutdown)

6.2.1 Reducing feed flows

Prior to stopping feed flow(s), the reformer production rate should be reduced in a controlled manner to a level that maintains process stability, but minimizes the impact of the feed flow stoppage on process equipment. The feed flow reduction rate shall be in accordance with plant operating procedures.

If hydrogen is being supplied to customers during this period, reformer firing should be reduced while maintaining the outlet temperature at a level that ensures adequate hydrocarbon conversion. Operators should carefully monitor key reformer parameters including reformer furnace pressure, fuel pressure, and excess oxygen. To prevent activation of a process interlock and total plant trip, control system actions and operator response shall ensure adequate steam flow is maintained as feed flow rates are reduced and eventually stopped.

As process feed flow is reduced, the portion of fuel that is recovered from or supplied by units downstream of the reformer (e.g., fuel from PSA tailgas) will decrease accordingly. Downstream unit shutdown and isolation procedures are performed in parallel with feed flow reduction and in accordance with plant operating procedures.

PAGE 16 AIGA 086/14

As feed flow(s) and product flow rate(s) decrease, product flow can be stopped and process gas directed to the appropriate flare or vent system.

6.2.2 Stopping feed flows

The actuation (closing) of valves to stop the flow of feed streams into the reformer shall be achieved through the control system. Feed valve closing can be achieved through:

- a low feed rate trip interlock activated as a result of the feed reduction;
- a switch or button engaged by the operator; and
- direct use of the feed flow control loop.

As feed flows are reduced, interlocks may have to be bypassed in order to continue the planned shutdown. Plant operating procedures shall address which interlocks may be safely bypassed.

Proper isolation of the feed streams shall be ensured through verification of closed valve positions (e.g., limit switch feedback, visual confirmation) once the control system action is complete. Manual isolation valves shall be closed according to the operating procedure. Timely completion of this step is necessary to avoid catalyst damage. Process pressure should be reduced to facilitate steam circulation, remove gas inventory from the unit, and prepare for nitrogen introduction.

Steam flow shall continue until replaced by nitrogen. Minimum steam flow may be ensured by a number of methods including:

- mechanical stop limit on the steam control valve;
- automated bypass around the steam control valve; and
- bypass line with orifice around the steam control valve.

If applicable, feed and/or product compressors may be shut down at this point in the procedure.

6.2.3 Reducing reformer firing

After stopping feed flow(s), reformer firing should continue at a significantly reduced rate. The continued firing will ensure a controlled reduction in process temperatures and pressures. Firing should be reduced in a manner that achieves a steady decrease of temperature in the reformer outlet components and convection section. A temperature decrease rate of 90 °F/hr (50 °C/hr) is provided as a guide.

The firing duty is further reduced to maintain the cool down rate as noted above. At a certain point, some burners will need to be isolated. The sequence of burner isolation shall be defined in the plant operating procedures and provide a balanced reduction in reformer firing to ensure burners with flame detectors are isolated last.

It is important to make frequent observations of the furnace interior through the inspection ports during reduced reformer firing. Emphasis shall be placed on burner, reformer tube, and reformer refractory inspections as described in AIGA 082/13 [4]. Interlocks may have to be bypassed as flows are reduced. Plant operating procedures shall address which interlocks may be safely bypassed.

6.2.4 Introducing nitrogen and stopping steam flow

As temperatures are reduced the risk of steam condensation and catalyst damage increases. Therefore, nitrogen is introduced to replace steam as the cooling fluid. A minimum nitrogen (or nitrogen plus steam) flow rate shall be maintained. See 5.2.1. A low flow (cooling fluid) combustion interlock should be active to prevent high reformer tube temperatures if flow is reduced or stopped.

Nitrogen is introduced to remove steam from the process piping and equipment. Nitrogen introduction points are determined by specific process designs. Process pressure must be reduced to allow the introduction of nitrogen. Once nitrogen flow is established and temperature is further reduced, process steam flow will decrease. Steam flow shall be stopped and isolated before reaching condensation temperatures in the catalyst

beds. As catalysts can be severely damaged by liquid water, the temperature limits with sufficient margin to avoid condensation should be clearly defined in the plant operating procedures.

Some plant designs include a nitrogen circulation loop. Operating procedures for these plants should address the line-up and startup of the circulation compressor. Other plants use nitrogen supplied from an external source. The nitrogen flows through the system and is vented (also called once-through nitrogen). A positive process pressure shall be maintained to avoid air ingress, which can cause catalyst damage.

6.2.5 Stopping fuel flow and isolation of fuel circuits

The firing duty is reduced further to maintain the cool down rate and burners are isolated as noted in 6.2.3.

When the minimum number of burners remain lit or a low flue gas temperature limit is reached, stop the fuel by closing the double block valves. The minimum number of burners depends on the reformer design. For example, it can be set by the number of flame detectors or the number of reformer sections. After the fuel is isolated, any remaining burner fuel valves can be closed. The cool down rate can be moderated by adjusting air flow through the furnace.

6.3 Unplanned shutdown

An unplanned shutdown is initiated by an input to the control system (e.g., manual pushbutton) or by a control logic action (interlock) resulting from an unexpected operating condition. The control actions taken are primarily determined by the failure position of automatic valves in the process, assigned shutdown settings of other control devices, and assigned shutdown positions of electrical circuit breakers.

There are a variety of causes for an unplanned shutdown, including:

- A process safety shutdown initiated by the SIS based on a logic output of instrumentation inputs;
- A machinery or equipment shutdown initiated by the control system, based on a logic output of instrumentation inputs; and
- A manual shutdown initiated by a push button or control system soft switch. Push buttons are typically located in areas of the plant (including the control room) that are easily accessible under emergency conditions.

After the unplanned shutdown is initiated, the control system shall put the reformer and associated process units into a safe shutdown condition. Based on the severity of the process condition, the control system initiates the appropriate actions. For example, if a reformer shutdown is initiated, the following actions typically occur:

- the fuel going to the reformer burners is automatically isolated;
- the feed system is automatically isolated and shutdown; and
- process gas is swept out of the reformer and other process units with steam and/or nitrogen and vented to a safe location.

After the unplanned shutdown has occurred, a list of immediate and subsequent actions shall be carried out by the operators. As the actions are carried out, the reasons for the shutdown are determined, the condition of the equipment is assessed, and the decision to continue the shutdown or complete a hot restart is made.

If the assessment is carried out quickly enough and the process conditions meet the criteria for a hot restart, the procedure described in 5.7.2 can be followed.

If the assessment requires a significant amount of time, or the process conditions no longer meet the criteria for a hot restart, the procedure for a cold restart shall be followed. If the decision is made not to restart, the following actions are typically carried out:

- isolate the feed systems at the battery limit;
- isolate the fuel systems at the battery limit;

PAGE 18 AIGA 086/14

 further isolate and/or depressurize other process units, assuring that reactive catalyst beds are properly blanketed with nitrogen; and

complete the shutdown procedures described in 6.2.

6.4 Isolation and purging of flammable gas systems in preparation for maintenance

Using a double block and bleed or block and blind, confirm all feed and fuel piping systems are isolated at the battery limit. If a flare equipped with a pilot burner exists and is needed for the disposal of flammable gases from other systems, verify flare pilot fuel and sweep gas source are available.

Nitrogen should be introduced into the flammable gas systems subject to maintenance. These systems should be purged through to a vent or flare system until the LEL measurement is below 25%, or to country-specific thresholds prescribed by governing regulations, or agreed to standard such as NFPA 56 (PS), *Standard for Fire and Explosion Prevention During Cleaning and Purging of Flammable Gas Piping Systems*, in the United States [6]. If toxic gases are present, the system shall be purged below the toxicity threshold as defined by country-specific government regulations.

A thorough and systematic method to ensure adequate purging of flammable gas circuits (including branches and dead legs) with verification of flammability or toxicity as noted above, should be outlined in the shutdown procedure and executed accordingly. The procedure may include a flow diagram for further illustration purposes.

If a flare is shared with another unit, the reformer flare header shall be purged and blinded at battery limit.

7 Training and procedures

Preparing operators to operate steam reformers requires a structured training package. Training typically includes basic information about the reformer operating technology, plant specific data (e.g., process and safety data), plant operating procedures, safety procedures, and maintenance requirements. The portion of the training that addresses startup and shutdown should be given by experienced personnel. Operators in training should spend significant time assisting an experienced operator before independently conducting a startup or shutdown.

It is extremely difficult to train personnel to recognize and react to unforeseen circumstances during a startup or shutdown. In addition, the infrequency of startup and shutdown of large hydrogen plants poses a challenge to maintaining operator competency in these tasks. The following techniques will help to ensure adequate personnel training:

- operators in training should spend significant time assisting an experienced operator during startups and shutdowns;
- simulation of the evolution of problem response in the form of a tabletop exercise;
- use of a process control simulator to allow operators to practice responding to a problem.

Operating procedures shall be in compliance with good industrial practice and regulatory requirements. The content of the procedures is further defined by company-specific requirements.

Typical components of plant operating procedures include:

- individual operating procedures for startup of significant pieces of equipment (e.g., compressors, pumps, items with subsystems);
- an overall startup procedure that covers the entire sequence and refers to other procedures or prerequisites as required (e.g., instrument air system);
- individual operating procedures for shutdown and isolation of significant pieces of equipment (e.g., compressors, pumps, items with subsystems);

an overall shutdown procedure that covers the entire sequence and refers to other procedures as required;
 and

a checklist of immediate and subsequent actions required after an unplanned shutdown to verify completion of the automatic sequence (e.g., introducing nitrogen, completing manual valve position changes).

8 References

Unless otherwise specified, the latest edition shall apply.

- [1] Code of Federal Regulations, Title 29 (Labor), Superintendent of Documents, U.S. Government Printing Office, 732 North Capitol Street, NW, Washington, DC 20401. www.gpo.gov/fdsys
- [2] Seveso III Directive 2012/18/EU, European Commission, Environment DG, B 1049, Brussels, Belgium. http://ec.europa.eu
- [3] AIGA 056/08, Safe Practices Guide for Cryogenic Air Separation Plants, Asia Industrial Gases Association, 3 HarbourFront Place, #09-04 HarbourFront Tower 2, Singapore 099254. www.asiaiga.org
- [4] AIGA 082/13, Combustion Safety for Steam Reformer Operation, Asia Industrial Gases Association, 3 HarbourFront Place, #09-04 HarbourFront Tower 2, Singapore 099254. www.asiaiga.org
- [5] AIGA 066/10, Selection of Personal Protective Equipment, Asia Industrial Gases Association, 3 HarbourFront Place, #09-04 HarbourFront Tower 2, Singapore 099254. www.asiaiga.org
- [6] NFPA 56, Standard for Fire and Explosion Prevention During Cleaning and Purging of Flammable Gas Piping Systems, National Fire Protection Association, 1 Batterymarch Park, Quincy, MA 02169. www.nfpa.org