

TARGET™ TAR REFORMING CATALYST FOR GASIFICATION PROCESS STREAMS

Richard Q. Long, PhD.
Senior Research Engineer
Nexceris, LLC

ABSTRACT:

Nexceris' *TARGET™* catalyst can convert waste tar to value-added syngas (CO and H₂) from gasified biomass through steam reforming and CO₂ reforming. As compared to conventional liquid scrubbing approach, this catalytic reforming method eliminates the process for liquid waste disposal and enhances overall energy efficiency.

In particular, the *TARGET™* base-metal catalyst is stable in the presence of H₂S and NH₃, two impurities in gasified biomass. Nearly 100% tar conversion has been achieved at 800-900°C during reforming of oak wood gasification product. The reforming activity did not change in 2000+ hours on stream in the presence of sulfur, allowing it to be loaded immediately downstream of biomass gasifiers to eliminate tar.

Furthermore, unlike conventional Ni-based reforming catalysts, Nexceris' *TARGET™* catalyst does not require pre-reduction process and can be self-activated in flowing biomass gasification gas at 700-850°C prior to operation. The demonstrated tar reforming performance, combined with design features that integrate well in gasified biomass system designs, creates unique value to system designers. *TARGET™* helps developers overcome a significant barrier for commercializing biomass gasification process, enabling efficient use of biomass to produce power, liquid fuels and valuable chemicals.



INTRODUCTION:

The benefits of biomass- and waste-derived gasification processes are compelling. Gasification technology provides syngas streams for renewable, low-carbon energy, fuels and chemical precursors. However, biomass and waste feedstocks are complex, containing a broad range of impurities and byproducts, including sulfur, ammonia and tar (a complex mixture of condensable hydrocarbons). The high boiling point (180-350°C) of tar results in condensation and polymerization of the material in exit pipes, heat exchangers, or particulate filters. In turn, this leads to choking and attrition that decreases system efficiency and increases process cost.

Nexceris engineers have developed a catalytic reforming approach to eliminate this challenge from gasification technology that is cost-effective and efficient. *TARGET™* catalysts convert tar to syngas, eliminating it as a condensable species. Compared to liquid scrubbing, *TARGET™* catalysts create a simpler and more energy efficient solution, while converting tar and light hydrocarbons to syngas (CO and H₂) that increase the fuel value.

TARGET™ PERFORMANCE:

To demonstrate the opportunity *TARGET™* catalysts can provide gasification users, tests were performed to show the catalyst's efficiency in destroying tars under a range of operating conditions.

The granular catalyst (35-60 mesh) was tested in a tubular reactor for reforming of oak wood gasification products¹. Toluene was used a probe of tar compounds and ethylene represented olefins. The gas hourly space velocities were 10,000-24,000 ml/g-hr. After the catalyst was loaded, it was heated to 750-850°C in the biomass gasification gas. The feed gas and product were analyzed on-line with a mass spectrometer.

The catalyst was also washcoated on a cordierite monolith with 400 CSPI channel density for reforming of methane, light hydrocarbons and tar (using naphthalene as a model compound) to syngas in a simulated biomass gasification product stream². The reaction conditions are 900 °C, GHSV = 10,000 h⁻¹. The gas composition was analyzed using a gas chromatograph (GC).

The testing results showed complete tar conversion was achieved at 800-850°C on granular *TARGET™* catalyst during reforming of oak wood gasification product (see Figure 1). The catalyst performance was also very stable during the testing; reforming activity did not change in 600 hrs on stream in the presence of sulfur (see Figure 2). Moreover, unlike other conventional Ni-based reforming catalysts, Nexceris' *TARGET™* catalyst does not need pre-reduction process and can be self-activated in flowing biomass gasification gas at 800-850°C prior to operation.

Reforming activities of hydrocarbons on *TARGET™*-washcoated monoliths are shown in Figure 3. C₂₊ hydrocarbon conversion reached 87 percent in the presence of H₂S, while methane conversion was approximately 20 percent. Hydrogen concentration in the product was 35 percent and H₂/CO ratio was ~1.8. For the C₂₊ hydrocarbons, propane and propylene were not detected in the product, indicating complete conversions. Approximately 85% of ethane and ethylene conversion was obtained.

¹ The gas compositions were 41.5% H₂O, 20.0% N₂, 13.5% H₂, 9.6% CO₂, 7.7% CO, 5.8% CH₄, 1.9% C₂H₄, 880 ppm toluene and 20 ppm H₂S.

² 14.4% H₂, 10.4% CO, 9.8% CO₂, 5.8% CH₄, 13.2% N₂, 44.6% H₂O, 1.6% C₂H₆ and C₂H₄, 0.2% C₃H₈ and C₃H₆, 30 ppm naphthalene (when used), 1000 ppm NH₃ and 22 ppm H₂S (when used)



TARGET™ Tar Reforming Catalyst for Gasification Process Streams

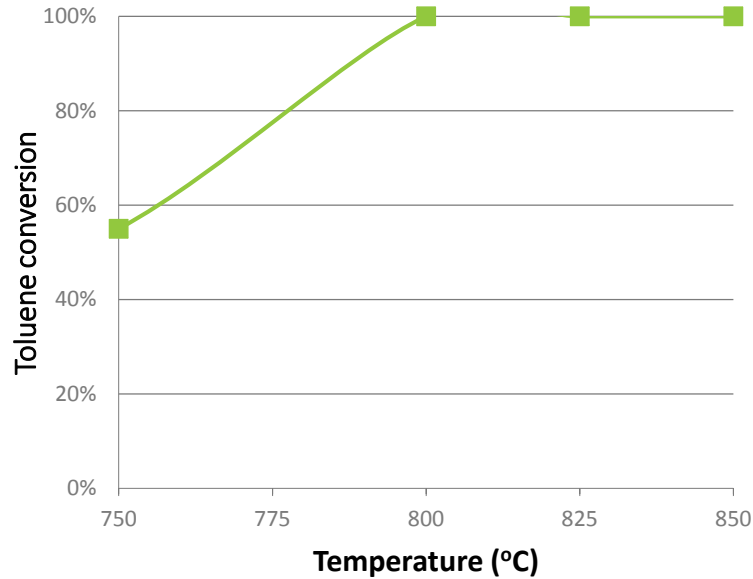


Figure 1. Tar reforming activity on granular *TARGET™* catalyst under the conditions of 41.5% H_2O , 20.0% N_2 , 13.5% H_2 , 9.6% CO_2 , 7.7% CO , 5.8% CH_4 , 1.9% C_2H_4 , 880 ppm toluene, 20 ppm H_2S and GHSV = 24,000 ml/g-h.

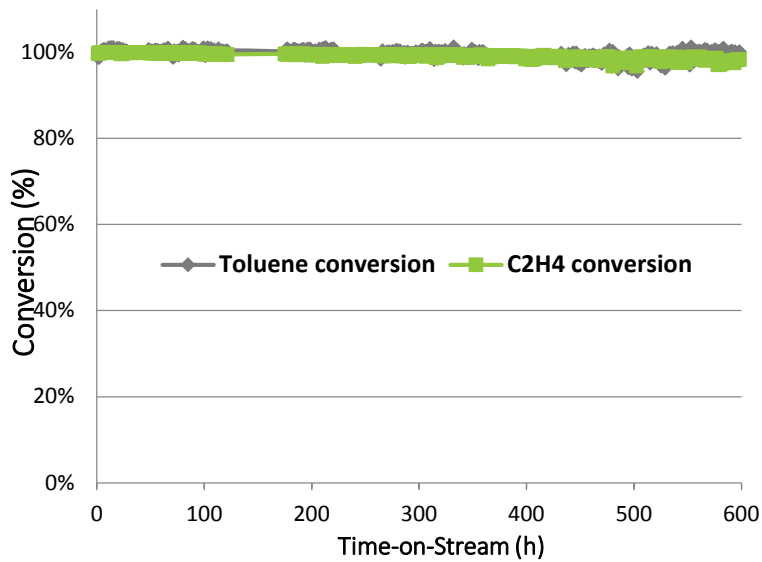


Figure 2. Preliminary lifetime on granular *TARGET™* catalyst under the conditions of 41.5% H_2O , 20.0% N_2 , 13.5% H_2 , 9.6% CO_2 , 7.7% CO , 5.8% CH_4 , 1.9% C_2H_4 , 880 ppm toluene, 20 ppm H_2S and GHSV = 10,000 ml/g-h.



*TARGET*TM Tar Reforming Catalyst for Gasification Process Streams

The above data indicate that the activity for reforming light hydrocarbons decreased in the following order C_3 hydrocarbons (100 percent) > C_2 hydrocarbons (85 percent) > methane (20 percent) on the *TARGET*TM catalyst-washcoated monolith. At 165 hours, 30 ppm naphthalene (a model tar compound) was added to the feed, but no change in catalytic performance was observed. Naphthalene was not detected in the exhaust by a mass spectrometer. The catalyst was tested for 500 hours in the presence of H_2S and no deactivation was observed (Figure 3).

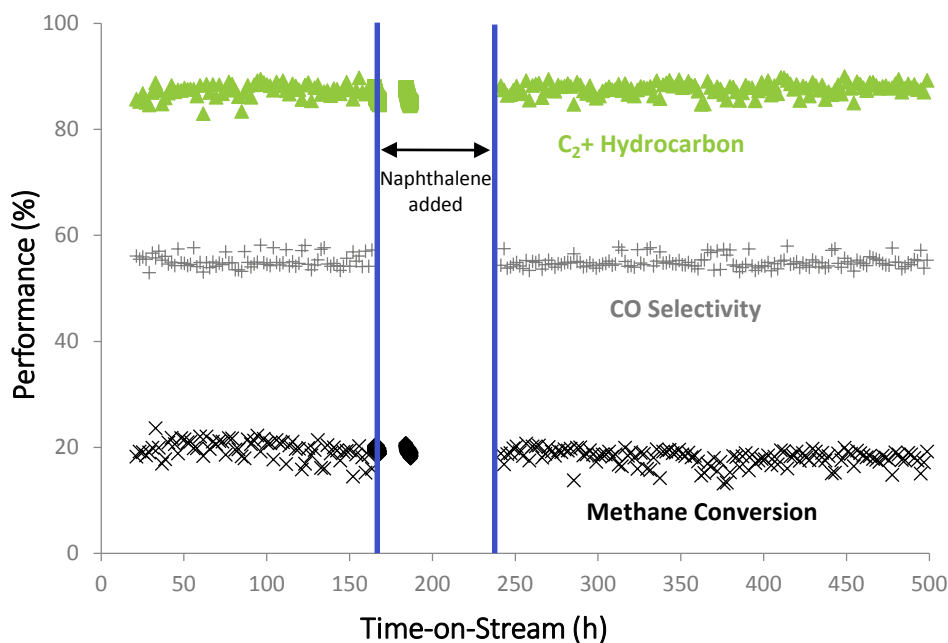


Figure 3. Reforming of biomass gasification products on a *TARGET*TM catalyst-washcoated cordierite monolith in the presence of H_2S under the conditions of 900 °C, GHSV = 10,000 h^{-1} , 14.4% H_2 , 10.4% CO , 9.8% CO_2 , 5.8% CH_4 , 13.2% N_2 , 44.6% H_2O , 1.6% C_2H_6 and C_2H_4 , 0.2% C_3H_8 and C_3H_6 , 30 ppm naphthalene (when used) and 22 ppm H_2S .

After the *TARGET*TM catalyst-washcoated monolith was tested for 1000 hours, 1000 ppm NH_3 was added to the feed while the other conditions were kept the same. It was observed that the addition of NH_3 did not impact the performance of the catalyst (see Figure 4). At 1145 hours, H_2S was removed from the feed stream while maintaining NH_3 concentration at 1000 ppm. C_{2+} hydrocarbon and methane conversions were increased to 100% and above 95%, respectively (Figure 4). H_2 concentration in the product was increased to 53% and H_2/CO ratio was approximately 2.7. The catalyst activity was almost identical to that in the absence of sulfur and ammonia. Additionally, the quick increase in C_{2+} hydrocarbon and methane conversions also suggests that H_2S has a reversible degradation effect on the catalyst. Upon H_2S removal, the catalytic performance was recovered quickly. This monolith catalyst was tested continuously for 2000+ hours in the presence of sulfur and no deactivation was observed.



TARGETTM Tar Reforming Catalyst for Gasification Process Streams

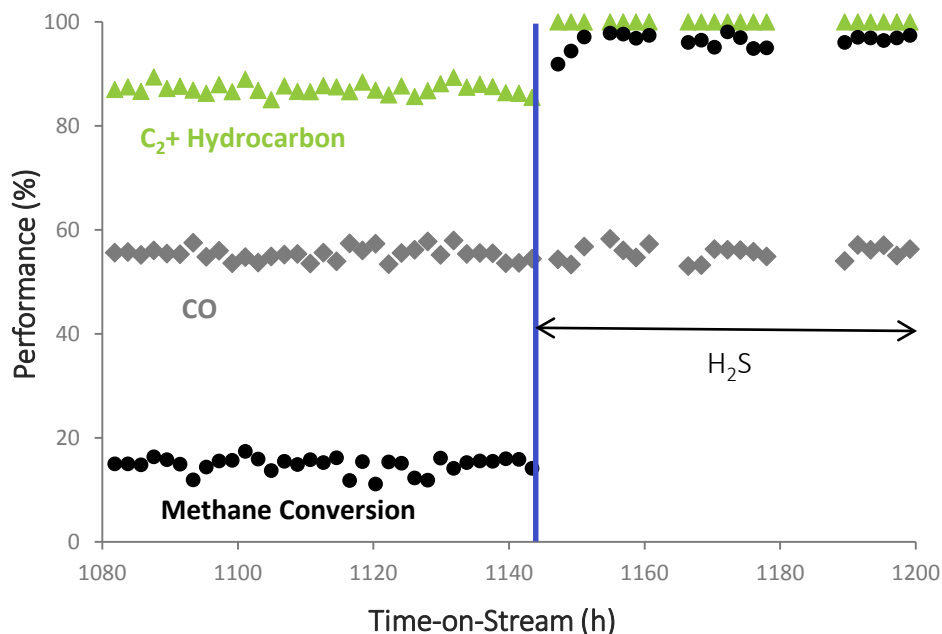


Figure 4. Reforming of biomass gasification products on a *TARGETTM* catalyst-washcoated cordierite monolith in the presence of NH₃ and H₂S under the conditions of 900 °C, GHSV = 10,000 h⁻¹, 14.4% H₂, 10.4% CO, 9.8% CO₂, 5.8% CH₄, 13.2% N₂, 44.6% H₂O, 1.6% C₂H₆ and C₂H₄, 0.2% C₃H₈ and C₃H₆, 1000 ppm NH₃ and 22 ppm H₂S (when used).

COMMERCIAL IMPLICATIONS:

TARGETTM offers a unique blend of design advantages to system developers—the catalyst integrates well thermally with gasifier systems, unlike other tar collection technologies, which require cooling of the gas stream to effectively operate. The demonstrated tolerance to sulfur completes this design advantage, as sulfur removal can occur after tar removal.

Unlike conventional Ni-based reforming catalysts, Nexceris' *TARGETTM* catalyst does not require pre-reduction process and can be self-activated in flowing biomass gasification gas at 700-850°C prior to operation. In addition, the *TARGETTM* catalyst is also very active in reforming light hydrocarbons to syngas.

Together with the demonstrated tar reforming performance, these design features create unique value to system designers. *TARGETTM* helps developers overcome a significant barrier for commercializing biomass gasification process, enabling efficient use of biomass to produce power, liquid fuels and valuable chemicals.

CONCLUSIONS:

Nexceris' *TARGETTM* catalyst can convert tar and hydrocarbons to syngas at high temperatures by steam reforming and CO₂ reforming. Stable in the presence of sulfur and ammonia, the catalyst achieves complete tar conversion at 800-850°C during reforming of oak wood gasification product, and has been demonstrated over 2,000 hours on washcoated monoliths. Further, *TARGETTM* has numerous design features that simplify its integration in gasification systems.