MATROSTECH

ALVIGO

Matros Technologies, Inc.

14963 Green Circle Dr.
St. Louis, Missouri 63017

www.matrostech.com
e-mail: info@matrostech.com

Phone: (314) 426-8620
Fax: (314) 426-8610

STEAM REFORMING CATALYSTS

Products overview, operating experience and performance comparison

High-performance catalysts are critical for synthesis gas processes technology. By partnering with ALVIGO, a leading Russian catalyst supplier, Matros Technologies makes it possible for customers worldwide to benefit from a range of catalysts that incorporate decades long Russian scientific tradition, unparalleled knowledge of our scientists and engineers, ISO 9001 compliant quality management system, and excellent customer service. With total annual output of 6,000 tons, we are able to meet the needs of the most demanding customers.

Catalysts **K-905-D1, NIAP-18 and NIAP-03-01** are designed for large multitubular steam reformers at ammonia, methanol, and hydrogen production plants. The catalysts are shaped as cylinders with single (NIAP-18, K-905-D1) or multiple holes (NIAP-03-01), flat (NIAP-18, K-905-D1) or convex base, and smooth or grooved (K-905-D1) side surfaces. Both promoted and non-promoted nickel oxide catalysts are available with supports made of corundum (α-alumina) or alumina / calcium aluminate.

The catalysts are used for both light (i.e., natural gas and associated gas) and heavy hydrocarbon feedstocks (i.e., LPG and naphtha) and can work at low steam/carbon ratio.

K-905-D1

Promoted nickel oxide catalyst supported on α-alumina. Used for severe operating conditions of low H_2O/C ratios, high heat-flux reformers with top-firing, and for heavy hydrocarbon feedstocks.

NIAP-03-01

Promoted or non-promoted, this nickel oxide catalyst is supported on α-alumina. Used for severe operating conditions of low H_2O/C ratios, high heat-flux reformers with top-firing, and for heavy hydrocarbon feedstocks.

FEATURES

Robust and efficient catalyst carriers

Active component is deposited on supports such as high-strength corundum (α-alumina) or calcium aluminate/alumina. High-temperature treated corundum support of NIAP-03-01 and K-905-D1 prevents formation of nickel spinel structures, thus ensuring high thermal stability and long life in the reformer. Low SiO_2 content, < 0.15 %, prevents problems related to silicon migration.

Calcium aluminate /alumina support of NIAP-18 catalyst increases surface alkalinity and promotes carbon removal reactions even in most severe operating conditions.

Proprietary rare earth metal oxide promoter

A proprietary rare earth oxide promoter suppresses carbon formation due to accelerating activation of water molecule. It ensures superior activity, coking resistance and thermal stability in applications with heavy hydrocarbon feedstocks, low steam/carbon ratio and highly intense top-fired furnaces.

Stable mechanical strength and performance

ALVIGO's catalyst manufacturing facilities carefully control mechanical strength and internal catalyst structure. Over 80 % of mechanical strength is retained after 4 years of operation.

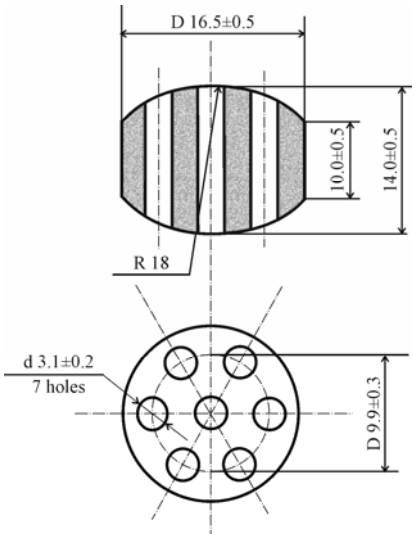
Catalysts retain high performance under severe, heavy-duty conditions of top-fired tube reformers.

Optimized pellet shape

K-905-D1 has six-flute cylindrical design that improves furnace pressure drop compared to older, Raschig rings shaped catalysts.

Advanced design of NIAP-03-01 comprises seven axial channels and rounded edges that facilitate loading and provide for higher bed density, critical for reactors with long narrow tubes.

The shape helps to increase feed gas flow rate or reduce methane slip. Maximum tube temperature can be reduced by up to 25 °C, with less than 60 °C temperature difference over the tube cross-section.



Design of NIAP-03-01 catalyst

Low sensitivity to process upsets

The catalysts are robust and easily tolerate various process upsets, such as:

- prolonged steam treatment at normal/reduced operating temperature
- formation of steam condensate at cold shutdowns
- hours long temperature increases of up to 1000 °C

Secondary reforming applications

Due to its high mechanical and thermal strength NIAP-03-01 performs well under severe conditions found in adiabatic reformers of ammonia production plants. An alternative is K-905-D2 catalyst, similar to K-905-D1 in shape and size, but specifically developed for these applications. When NIAP-03-01 and/or K-905-D2 make up the bulk of secondary reformer catalyst bed, process gas composition at the outlet is essentially at thermodynamic equilibrium. These catalysts help reduce bed volume, while increasing void portion and improving air/gas mixing above the bed.

NIAP-22

29.5 mm diameter nickel oxide catalyst supported on α-alumina applied as guard bed in large secondary reformers.

NIAP-20-01

Secondary reforming catalyst based on nickel oxide catalyst supported over calcium aluminates. Used in ammonia plants with capacity up to 1,500 tons/day.

In commercial secondary reformers, NIAP-03-01 and K-905-D2 are loaded solely, or in combination with ALVIGO's guard bed catalysts NIAP-22 and NIAP-20 (rings, 19-20 mm in diameter). A guard bed placed on top of the main bed provides for enhanced gas distribution and mixing throughout the reformer's cross section.

NIAP-03-01

Principal technical characteristics of NIAP-03-01 compare favorably to similar commercial catalysts from other major manufacturers, as illustrated by Table 1. It does not require pre-reduction in front layers,

unlike catalyst A, and provides for higher bed surface area – and higher performance - than that of catalyst B. At the same time, optimized shape and size of NIAP-03-01 pellets helps to maintain bed pressure drop on par with alternative catalysts.

NIAP-03-01 possesses excellent mechanical strength while the shape of its pellets provides for high void fraction and specific surface area of the bed. Proprietary lanthanum oxide promoter improves catalytic activity, which helps to operate a reformer at an optimum temperature, and to retain high selectivity over a longer catalyst lifetime. Combination of properties makes it possible to operate a reformer at high load without overheating tube walls and at low pressure drop.

Table 1. Technical parameters of NIAP-03-01 as compared to the competing products.

Catalyst	NIAP-03-01	A	B	C
Number of holes	7	7	4	1+9
Carrier	α-alumina	Mg-spinel	Ca polyaluminates	α-alumina
Size, mm (D×d×h)	16.5 × (7) 3.0 × 14.0	16.7 × (7) 3.3 × 11.0	13.9 × (4) 3.9 × 19.1	19 x (9) 1.8 x 16
Bulk density, kg/l	0.93	0.95	0.9	1.2
Ni content, % wt.	> 12	> 16	> 15	> 12
Bed void fraction, m^3/m^3	0.55	0.56	0.56	0.57
Bed surface area, $m^2/m3$	410	400	380	330

COMMERCIAL EXPERIENCE

Commercial Systems Overview

ALVIGO catalysts for primary and secondary reforming have been successfully operating in 20 ammonia plants with daily capacity of 1,360 to 1,700 metric tons, two large methanol plants with annual capacity of 750,000 metric tons, and in several hydrogen plants producing up to 20,000 metric tons of H_2.

Table 2. Most recent applications of NIAP-03-01 catalyst in Russian ammonia plants.

Type of reformer	Number of tubes x diameter x length	Catalyst volume, m^3	Catalyst charge since
Ammonia, Foster Wheeler design	426 x 89 mm x 14 m	35.3	1998
Ammonia, M. W. Kellogg design, 3 plants	504 x 72 mm x 10.8 m	20.8	2002
Ammonia, M. W. Kellogg design, 3 plants	504 x 85 mm x 10.8 m	29.2	1999

Table 3 presents operating parameters for three M.W. Kellogg reformers loaded with NIAP-03-01 catalyst. The catalyst works for 3 – 4 years in those plants, despite many operational upsets such as steam condensation and cold shutdowns. During the lifetime, the catalysts provide for 9 – 11 % of CH_4 at the outlet.

Table 3. Performance of commercial tubular reformers using NIAP-03-01 after one year of operation

Plant	SALAVAT NEFTEORGSYNTEZ	TOGLIATTI AZOT	NOVOMOSKOVSKI AZOT
Ammonia capacity, mtpd	1,650	1,360	1,450
No. of tubes x diam. x length	504 x 72 mm x 10.8 m	504 x 72 mm x 10.8 m	504 x 85 mm x 10.8 m
Gas flow rate, nm^3/hr	46,000	38,000	40,200
Steam : gas ratio	3.4	3.75	3.7
Process pressure, MPa gauge	3.1	2.92	3.06
Inlet feed temperature, °C	463	468	470
Outlet ~~collector~~ header temperature, °C	785	790	775
CH_4 outlet, dry gas, % vol.	10,0	9.3	10.2
Reformer pressure drop, MPa	0.22	0.18	0.17

In secondary reformers loaded with NIAP-03-01, typical operating conditions include temperatures reaching 1,250 °C at the bed inlet, and 1,030 °C at the outlet, pressures up to 3.5 MPa, and air/carbon ratios of 1.35 - 1.45. The outlet concentration of methane is maintained under 0.15 - 0.35 %. The catalyst charge typically lasts in excess of 4 years.

Long Catalyst Lifetime

At the NOVOMOSKOVSKI AZOT ammonia plant, the ring-shaped NIAP-18 catalyst has been serving continuously for about 11 years without replacement. **Table 4** presents average process parameters collected during 1993-2004. The record lifetime was achieved in a Kellogg furnace that holds 20.8 m^3 of catalyst and operates at natural gas flow rate of 36 - 38 KNm^3/hr and steam/gas ratio of 3.5 - 3.8. At the end of the run, the catalyst has shown no sign of activity decrease. The pressure drop increased from 2.6 to 4.1 kgf/cm^2, because of moderate catalyst deterioration caused primarily by process shutdowns.

Reformer operation parameters

Ammonia capacity, metric tons/day	**1,365**
Furnace type	M. W. Kellogg design, 504 tubes, 72 internal diameter
Concentration of sulfur in natural gas feed, ppm	0.1-0.2
Number of plant shutdowns from 1993 to 2003	20

Table 4. Record performance of NIAP-18 catalyst in a primary reformer

Year	1993	1994	1995	1996	1997	1998
Natural gas feed flow rate, Nm^3/hr	36,000	35,900	36,400	36,200	36,500	36,700
Pressure in furnace inlet, kg_f/cm^2	33	32	32	32	30	31.5
Steam/gas ratio	3.7	3.7	3.5	3.6	3.7	3.9
Outlet furnace temperature, °C	798	805	802	810	815	811
Outlet concentration of CH_4, % vol. dry gas	8.2	8.2	8.8	8.0	8.8	7.6
Reformer pressure drop, kg_f/cm^2	2.60	2.77	2.94	3.11	3.30	3.40

Table 4. Record performance of NIAP-18 catalyst in a primary reformer (continued)

Year	1999	2000	2001	2002	2003	2004 March
Natural gas feed flow rate, Nm^3/hr	36,600	37,100	38,400	38,500	36,500	36,000
Pressure in furnace inlet, kg_f/cm^2	31.5	32	33	32	33	32
Steam/gas ratio	4.0	3.6	3.6	3.6	3.7	3.7
Outlet furnace temperature, °C	810	812	810	805	809	811
Outlet concentration of CH_4, % vol. dry gas	7.2	7.2	7.7	8.1	7.8	8.5
Reformer pressure drop, kg_f/cm^2	3.60	3.60	3.60	4.10	4.10	4.10

Performance Comparison between NIAP-03-01 and Competition Catalyst C

A Russian plant with two essentially identical reformers has been using both NIAP-03-01 and a catalyst **C** from a Western European supplier for several years. Performance data collected from 1996 to 2004 are given in Table 5.

Table 5. NIAP-03-01 and catalyst C commercial performance comparison.

Plant	**Russian ammonia plant**	
Production capacity, metric tons/day	1,360	
Type of reformer	Foster Wheeler	
Number of tubes x diameter x length	426 x 89 mm x 14 m	
Catalyst volume, m^3	35.3	
Catalyst type	**C**	**NIAP-03-01**
Catalyst dimensions: diameter x (number of holes) diameter of holes x length	19 x (9)1.8 x 16	16.5 × (7) 3.0 × 14.0
Gas flow rate, Nm^3/hr	32,400	30,800*
Steam : gas ratio	3.7	3.8
Gauge pressure, MPa	3.1	3.1
Inlet feed temperature, °C	510	501
Outlet concentration of CH_4, % vol.	10.4	9.4
Reformer pressure drop, MPa	0.22	0.14
Catalyst usage	1996-2002	Without replacement from August 1998

* according to latest 2004 data, the flow rate was 36,500 Nm^3/hr at steam/gas ratio of 3.6.

By the end of its service in 2002, the catalyst **C** has been coked and deactivated, having caused massive increase in outlet methane concentration and pressure drop. Under similar operating conditions, NIAP-03-01 has demonstrated stable performance for almost 6 years. Most recent data obtained in 2004 showed outlet concentration of methane at less than 11.7 % (at 759 °C furnace outlet temperature) and pressure drop not exceeding 1 kgf/cm^2.

Matros Technologies, Inc.
14963 Green Circle Dr.
St. Louis, MO 63017, USA.
www.matrostech.com

fax. +1-314-426-8610
tel. +1-314-426-8620
e-mail: info@matrostech.com