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Investigation of Syngas Production from Waste Gas and Ratio Adjustment using a Fischer-Tropsch Synthesis Reactor

E.Darzi

***Abstract*—**In this study, a reformer model simulation to use refinery (Farashband refinery, Iran) waste natural gas. In the petroleum and allied sectors where natural gas is being encountered (in form of associated gas) without prior preparation for its positive use, its combustion (which takes place in flares, an equipment through which they are being disposed) has become a great problem because of its associated environmental problems in form of gaseous emission. The proposed model is used to product syngas from waste natural gas. A detailed steady model described by a set of ordinary differential and algebraic equations was developed to predict the behavior of the overall process. The proposed steady reactor model was validated against process data of a reformer synthesis plant recorded and a good agreement was achieved. H_2/CO ratio has important effect on Fischer-Tropsch synthesis reactor product and we try to achieve this parameter with best designing reformer reactor. We study different kind of reformer reactors and then select auto thermal reforming process of natural gas in a fixed bed reformer that adjustment H_2/CO ratio with CO_2 and H_2O injection. Finally a strategy was proposed for prevention of extra natural gas to atmosphere.

***Keywords*—**Fischer-Tropsch, injection, reformer, syngas, waste natural gas.

I. Introduction

ABOUT 100 billion cubic meters of natural gas are burned off or simply vented at remote oil rigs and refineries that are not connected by pipelines. It is becoming unacceptable to flare associated gas from oil fields. The practice wastes a precious fuel and pumps methane, a potent greenhouse gas, into the atmosphere [1]. In the crude oil producing sectors, there is a need also for a perfect knowledge of anticipated gaseous emissions from associated natural gas of known composition being flared on daily basis through combustion activities under several operating conditions. This will help in the control of gaseous emissions from these flares and thus in the protection of their immediate and distant environment against environmental degradation via air pollution. The non-methane gaseous emissions resulting from natural gas combustion and which are of environmental concern include oxides of nitrogen, carbon dioxide, and carbon monoxide. Routine flares in the country should be minimized for gaseous emission reduction [2]. So, researchers have been looking for viable technologies to convert the natural gas found at small, isolated oil fields into compounds that are easier to transport and distribute. The process will also face competition. New gas-to-liquids technology, which converts natural gas into synthetic liquid fuels, is starting to become popular as an alternative to liquefied natural gas, and it's garnering the attention of oil giants like Exxon and Shell [1]. Gas to Liquids (GTL) conversion is an umbrella term for a group of technologies that can create liquid hydrocarbon fuels from a variety of feed stocks. The conversion of natural gas into liquid fuels is an attractive option to commercialize abundant gas reserves [3]. Moreover, synfuels may have a premium value because they are sulphur-free and because they have high cetane or octane numbers [4].During the last couple of years, there has been a renewed interest in the use of Fischer–Tropsch technology for the conversion of natural gas to liquids. Some of the factors that contributed to this are:

- An increase in the known reserves of natural gas.
- The need to monetize remote or stranded natural gas.
- Environmental pressure to minimize the flaring of associated gas.
- Improvements in the cost-effectiveness of Fischer–Tropsch technology resulting

The process to convert natural gas to liquids can be divided into three process steps:

- Syngas generation
- Syngas conversion
- Hydroprocessing

The choice of reformer technology will have an influence on the thermal efficiency of the plant as a whole and on the capital costs of the reformer, oxygen plant where applicable and the Fischer–Tropsch section. An obvious advantage of steam reforming is that its does not need an oxygen plant. However, since steam reformers are more costly than either POX or auto thermal reformers, there is a minimum plant size above which the economy of scale of a cryogenic oxygen plant in combination with a POX or auto thermal reformer is cheaper than a steam reformer on its own. The industrial gas industry has in the last decade shown increasing interest in ATR for economic production of H_2 and CO or CO-rich mixtures, in particular when low cost oxygen is available. Large-scale conversion of natural gas into liquid products may play an important role in the energy economy. A key parameter is the cost of the manufacture of synthesis gas. Today ATR appears to be the cheapest solution fulfilling the optimum requirements of the MeOH and FT syntheses [4].In

Young Researchers Club Kashan Unit, Iran..E-mail: elahe_darzi@yahoo.com

this work try to use ATR reformer that product syngas. Manipulating the operating conditions (temperature, pressure and gas composition) can control the product spectrum of the Fischer–Tropsch process. Since the H_2 /CO ratio of the syngas is an important design variable to maximize the production of high quality diesel, the designs of the reformer and the Fischer–Tropsch sections can not be done in isolation. The most cost-effective design for both units can only be obtained by taking the mutual interaction between these units into account.

II. PROBLEM FORMULATION

A. Fixed- bed steam reforming reactor

In GTL technology, FT conversion process is employed which requires a specific molar ratio of hydrogen depending upon the product. In methane steam reforming, the catalytic fixed-bed reactor is fed with a gas mixture of CH_4 and H_2O in a molar ratio from 1:3 to 1:4. Commercial catalyst is composed of nickel supported on alumina and the reactor consists of vertical tubes (between 10 and 900) with internal diameters from 7 to 16 cm and lengths from 6 to 12 m, inserted in a radiant furnace chamber. The feed conditions are about 600 ^{0}C and from 1.5 to 3.0 MPa. The maximum temperature that the reactor can stand is limited by the metallurgical limitations of the tubes, since at higher temperatures the metal tubes can creep under stress [5]. Table 1 presents the characteristics of the fixed bed reactor developed by South Pars [6]. A one-dimensional and heterogeneous model comprising a set of heat and mass transfer equations and the kinetics of the main reactions is chosen in this work to simulate the fixed bed steam reforming reactor. The major assumptions in the model can be listed as follows:

1. Ideal gas behavior
2. Non-isothermal conditions
3. Mass axially dispersed plug-flow conditions are considered with negligible radial gradients.
4. Thermal dispersion in the axial direction is also considered with negligible radial gradients
5. Concentration and temperature gradients in the radial direction are ignored.
6. No temperature gradient in the catalyst particles.
7. Six reactive species (CH_4, CO, CO_2, H_2, and H2O) and one inert component (N_2) are involved in the model.
8. Uniform particle size.
9. Constant bed porosity.

Reactor has been modeled:

The mass and energy equations for the bulk gas phase can be written as follows:

$$\frac{-f_{t0}}{A_z}\frac{dy_i}{dz} + a_v c_t k_{gi}(y_{is} - y_i) = 0 \quad \text{i=1,…N-1} \tag{1}$$

$$\frac{-f_{t0}}{A_c} c_{pg}\frac{dT}{dz} + a_v h_f (T_s - T) + \frac{\pi D_i}{A_c} U_{shell}(T_{shell} - T) = 0 \tag{2}$$

Where, y_i and T are the gas-phase mole fraction and temperature, respectively.

The boundary conditions for the bulk phase are expressed by:

At z=0 $y_i=y_{i,in}$,$T=T_{in}$

The mass and energy balance equations for the catalyst pellets can be formulated as follows:

$$k_{gi} a_v c_t (y_i - y_{is}) + \rho_B \eta r_i = 0 \quad \text{i=1,…N-1} \tag{3}$$

$$a_v h_f (T - T_s) + \eta \rho_B \sum_{j=1}^{8} r_j \left(-\Delta H_{fj}\right) = 0 \tag{4}$$

Where, y_{is} and T_s are the mole fractions on the catalyst surface and solid-phase temperature, respectively.

B. Simulation of the Reformer (ATR)

SR is a highly endothermic process and therefore demands an efficient heat supply to the system. It is usually operated in a temperature range of 850–950 ◦C on Ni-based catalyst. It is a very energy- and capital-intensive process although the present technology approaches 90% of the maximum thermodynamic efficiency. However, steam reforming is economically unattractive option for low-volume and low-pressure hydrogen production. We select ATR in this simulation. Although ATR has an interesting potential in industrial application, there has been only a limited amount of work reported in the field of reactor design and simulation [7].ATR combines the effects of both the endothermic steam reforming and the exothermic partial oxidation by feeding the fuel together with the oxidant (air fed or oxygen fed) and steam over a catalyst in a fixed bed reactor.

C. Reformer Equations

The reformer equations are solved, and in addition, the reactor input flow rate and compositions are also corrected.Mass and energy balances in the gas phase:

$$\frac{\partial(uC_i)}{\partial z} + k_{gi} a_v (C_i - C_{i,s}) = 0 \tag{5}$$

$$u\rho_f c_{pg}\frac{\partial T}{\partial z} - h_f a_v (T_s - T) = 0 \tag{6}$$

Mass and energy balances in the solid phase:

$$k_{gi}(C_i - C_{i,s}) - (1 - \varepsilon_b)\rho_{cat} r_i = 0 \tag{7}$$

$$h_f a_v (T_s - T) - \rho_{cat}(1 - \varepsilon_b)\sum -\Delta H_j \eta_j R_j = 0 \tag{8}$$

Boundary conditions:

At the reformer inlet $z = 0$:

$C_i=C_{i,0}$ $T=T_0$ $T_s=T_{s,0}$

At the reformer exit z = L:

$$\frac{\partial C_i}{\partial z} = 0 \qquad \frac{\partial T}{\partial z} = 0 \qquad \frac{\partial T_s}{\partial z} = 0$$

Initial conditions:

$C_i=C_{i,0}$ $T=T_0$ $T_s=T_{s,0}$

D.Reaction Network

The steam reforming components include H_2, CO, CO_2, H_2O, CH_4, and N_2. The following reactions are considered as dominate steam reforming reactions [5]:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad (R1)$$

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \quad (R2)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (R3)$$

The reaction rate equation is as follows:

$$R_1 = \frac{k_1}{p_{H2}^{2.5}}\left(p_{CH4}p_{H2O} - \frac{p_{H2}^3 p_{CO}}{K1}\right) \times \frac{1}{DEN^2} \quad (9)$$

$$R_2 = \frac{k_2}{p_{H2}^{3.5}}\left(p_{CH4}p_{H2O}^2 - \frac{p_{H2}^4 p_{CO2}}{K2}\right) \times \frac{1}{DEN^2} \quad (10)$$

$$R_3 = \frac{k_3}{p_{H2}}\left(p_{CO}p_{H2O} - \frac{p_{H2}p_{CO2}}{K3}\right) \times \frac{1}{DEN^2} \quad (11)$$

In a reforming process of natural gas, many reactions are likely to occur. If we consider that methane is the major dominating species in natural gas, nine reactions will be involved. The first four reactions are considered as the prevailing reaction routes in the auto thermal reforming process [7].

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad (R4)$$

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \quad (R5)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (R6)$$

$$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O \quad (R7)$$

The reaction rate equation is as follows :
R_4, R_5, R_6 in SR.

$$R_4 = \frac{k_{4a}p_{CH4}p_{O2}}{(1+K_{CH4}^c p_{CH4}+K_{O2}^c p_{O2})^2} + \frac{k_{4b}p_{CH4}p_{O2}}{1+K_{CH4}^c p_{CH4}+K_{O2}^c p_{O2}} \quad (12)$$

Therefore, the reaction rate of each species becomes:

$$r_{CH4} = -\eta_1 R_1 - \eta_2 R_2 - \eta_4 R_4 \quad (13)$$

$$r_{O2} = -2\eta_4 R_4 \quad (14)$$

$$r_{CO2} = \eta_2 R_2 + \eta_3 R_3 + \eta_4 R_4 \quad (15)$$

$$r_{H2O} = -\eta_1 R_1 - 2\eta_2 R_2 - \eta_3 R_3 + 2\eta_4 R_4 \quad (16)$$

$$r_{H2} = 3\eta_1 R_1 + 4\eta_2 R_2 + \eta_3 R_3 \quad (17)$$

$$r_{CO} = \eta_1 R_1 - \eta_3 R_3 \quad (18)$$

$\eta_1 = 0.07$, $\eta_2 = 0.06$, $\eta_3 = 0.7$, $\eta_4 = 0.05$

III. Problem Solution

The governing equations of this model form a set of differential algebraic equations which is consisted of the equations of mass and energy conservative rules of both solid and fluid phases in reactor. Backward finite difference approximation is applied here to solve this set of equations. The obtained nonlinear algebraic equations are a boundary value problem and have been solved using the shooting method. The shooting method converts the boundary value problem to an initial value one. The solution is possible by trial and error method, reactor is divided into 30, and then Gauss-Newton method is used to solve the non-linear algebraic equations in each node. In order to verify the goodness of the reactor model, simulation results were compared with the historical process data of a conventional steam reforming reactor under the design specifications and input data in Table1. The predicted results of production rate and the corresponding observed data of the plant are presented in Table. 2. It was observed that the model performed satisfactorily well under industrial conditions and there was a good agreement between plant data and the simulation data.

TABLE 1
STEAM REFORMING PILOT PLANT CHARACTERISTICS [6]

Parameter	Value
Tube diameter(cm)	12.5
Molar ratio of CH_4/H2O feed	0.55
Feed temperature [K]	793.15
Reactor pressure [bar]	40
Catalyst sizes [mm]	16×19
Catalyst density [kg.m^{-3}]	1870
Bulk density[kg.m^{-3}]	800
Number of tubes	184
Tube length[m]	5
Bed voidage	0.4
Feed molar flow rate[mol/s]	13.783

TABLEII
COMPARSION BETWEEN MODEL RESULTE WITH PILOT PLANT DATA FOR FRESH [7]

parameter	Pilot Plant	Predicted	Error %
CH_4	20.41	25.84	26.60
CO_2	5.71	6.02	5.72
CO	3.15	2.17	-31.11
H_2O	38.05	47.51	24.86
H_2	31.39	29.55	-5.861

Synthesis gas routes are capital intensive and hence there is a great interest in optimizing process schemes based on steam reforming and auto thermal reforming as well as exploring new principles for manufacture of synthesis gas [4].H_2/CO ratio has important role in GTL process. We compare SR reactor and ATR reactor to product desirable H_2/CO. Fig.1 and Fig.2 have been shown H_2 and CO mole fraction along two kind of reactor. According these Figures and advantages of ATR reactor that mention previously we select ATR reactor for our simulation.

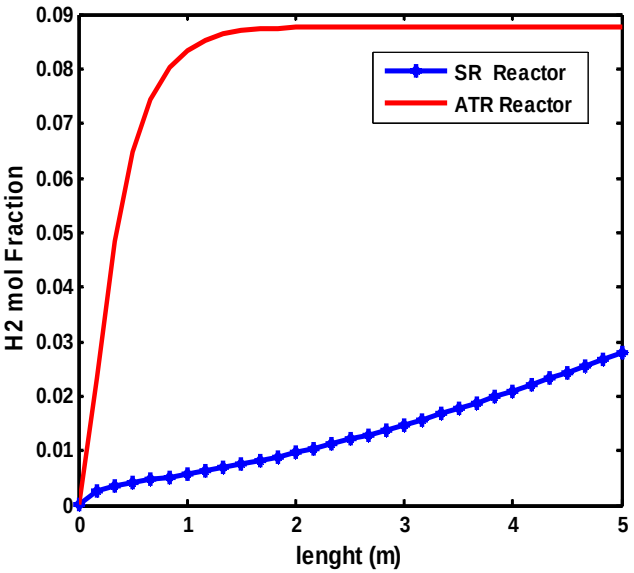

Fig.1 Comparison of H_2 mole fraction along ATR and SR reactors

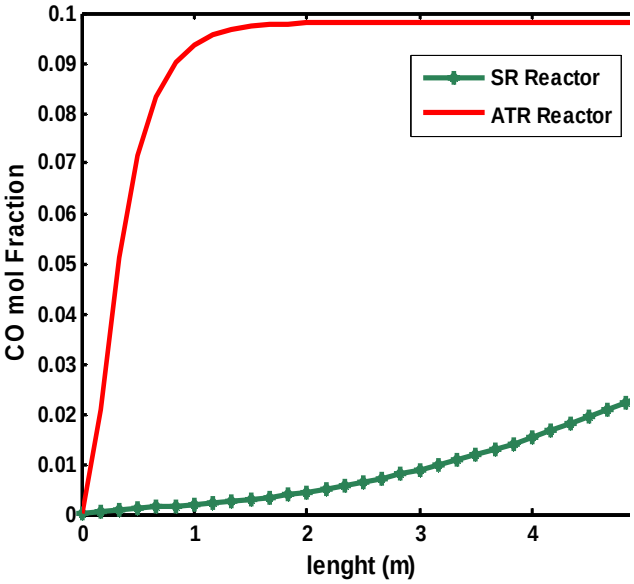

Fig. 2 Comparison of CO mole fraction along ATR and SR reactors

ATR reformer reactor:

Refinery waste natural gas enters to ATR reformer to product synthesis gas for Fischer-Tropsch synthesis reactor.H_2/CO has important role in GTL process. We injected steam and CO_2 to feed gas that we reach enough H_2/CO ratios. Figs. 3.4.5 show the CH_4 and CO and H_2 composition distribution during auto thermal reforming at thermodynamic equilibrium at a pressure of 68.95 bar .Conversion levels greater than 96% can be achieved at temperatures above 500 ◦C. However, we preheat feed gas from 30 ^{0}C until 520^{0}C.Feed component increase in reactor entrance because recycle flow that contain unreacted gas is recycled to reactor. Algebraic and differential equations of steady-state model reformer were solved according to the procedure mentioned previously. Figures show the mole fraction of reactants and products along the reactor results from steady-state simulation. Fig. 3 shows the mole fraction profile of methane along the reactor while Figs. 4.5 illustrate similar results for H_2 and CO. As can be seen from these figures, H_2 and CO mole fractions increase while methane mole fraction decreases along the reactor. Fig. 6 reveals how the ATR process behaves under the given simulated conditions in terms of heat transfer. Fig. 6 depicts the temperature profiles along the reformer at steady state in the gas and solid phases. It is evident that heat transfer is quite effective and the interfacial resistances between the catalyst and the gas are relatively small along the reformer, although the catalyst surface is about 11 ◦C higher in temperature than the bulk gas at the front section. This is due to the fact that heat of combustion generated in the catalyst is effectively transported to the bulk gas. The two profiles are almost identical after the first 20% of the reformer length. Similarly, the interfacial concentration gradients are found to be negligible due to effective mass transport in the gas film.

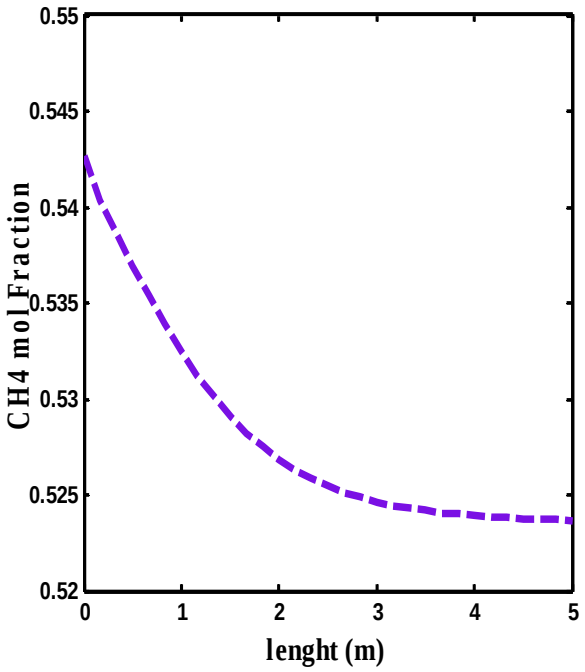

Fig. 3 CH4 concentration profile along the ATR reformer

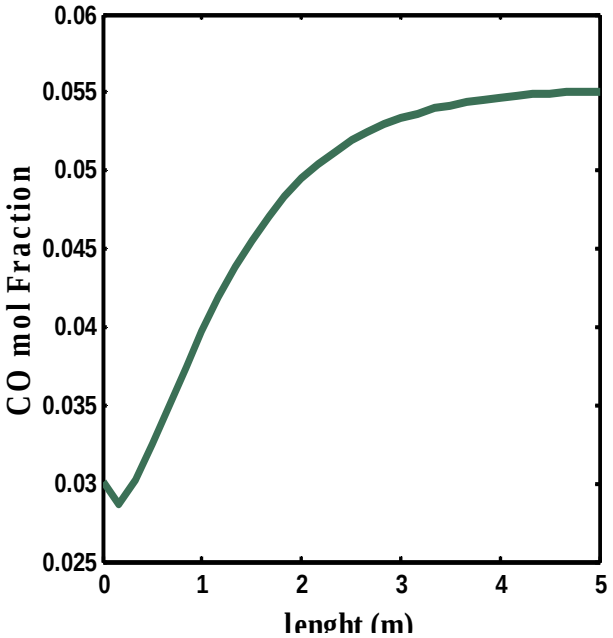

Fig. 4 CO concentration profile along the ATR reformer

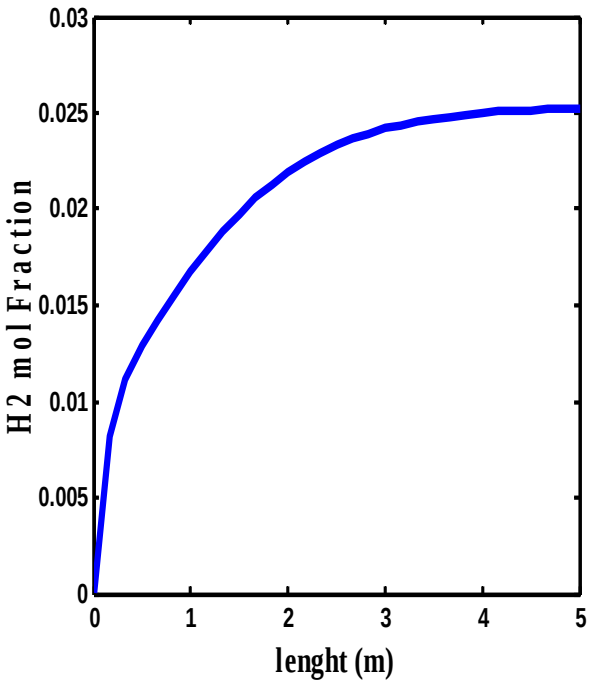

Fig. 5 H_2 concentration profile along the ATR reformer

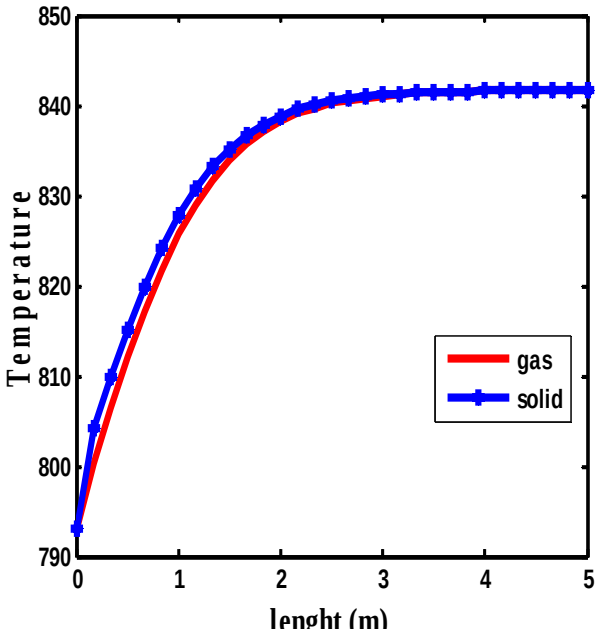

Fig. 6 Reacting gas temperature along the ATR reformer reactor

IV. Conclusion

Gaseous emissions from combustion of natural gas are of great environmental concern. While CO_2 is a' green house'' gas, CO and NO are know to have severe health impact on man. An industrial GTL synthesis loop was modeled. This simulation carries out to consume waste natural gas in refinery. Several optimal policies have been explored in order to compensate for conversion waste gas to syngas. The mathematical model was validated against the pilot plant data. In the design of GTL synthesis loop reformer has important role. H_2/CO ratio has important effect on Fischer-Tropsch synthesis reactor product. In this study show that ATR reforming is better than steam reforming for GTL process. We use fixed bed ATR reactor that H_2O and CO_2 injected so that H_2/CO ratio was desirable for Fischer-Tropsch synthesis reactor. This feature suggests that the concept of GTL loop system is an interesting candidate for producing gasoline or lighter hydrocarbons from natural gas.

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