Hot Gas Clean-Up with Dolomite
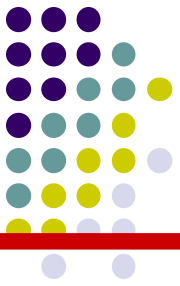
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TUBITAK Marmara Research Center, Energy Institute, Turkey
*Istanbul Technical University, Chemical Engineering Department, Turkey

EERA bed materials workshop
Istanbul, 18 April 2012

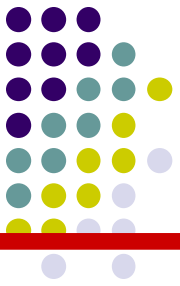# Outlines

Introduction

Motivation

Objectives

Experimental

Results and Discussions

Conclusions

Introduction

◈ Energy

> ➤ any source of usable power
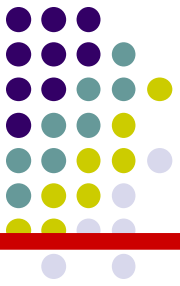> ➤ one of important needs of human beings

◈ Energy usage today

> ➤ global problem with catastrophic consequences

◈ Coal & Oil

> ➤ Two biggest energy sources of world today
> ➤ causes serious environmental problems

Introduction

◈ For Turkey

- ➢ Sustainability and security of the energy supplying is a common problem for many countries including Turkey (Indeed for all countries).

- ➢ Coal and biomass are the most widespread indigenous energy sources of Turkey.

- ➢ Therefore, developing know-how on the clean utilization of coal and biomass is of great importance.
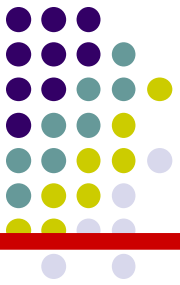
Introduction
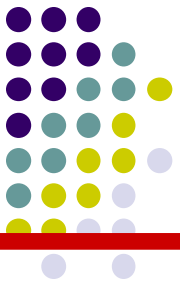
◈ Average characteristics of Turkish lignites

Reserve	12.1 billion tons
Average moisture content	42 %
Average ash content	21.5 %
Average sulfur content	1.85 %
Average calorific value	1807 kcal/kg (7553 kJ/kg)

high moisture

high ash

high sulfur content

low calorific values

} Low grade fuel

2001-3000 kcal/kg
3001-4000 kcal/kg
>4000 kcal/kg
<1000 kcal/kg
1000-2000 kcal/kg
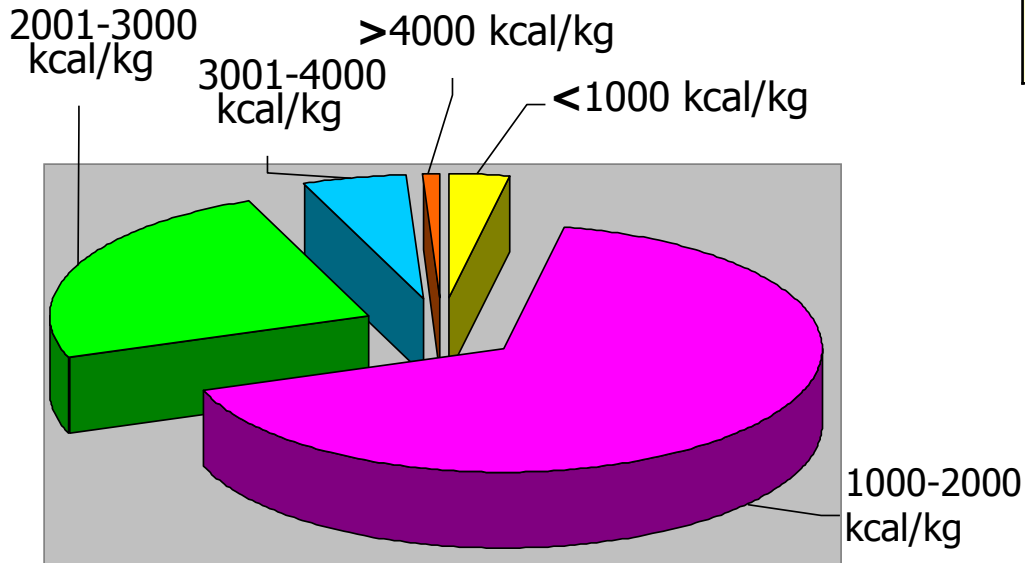
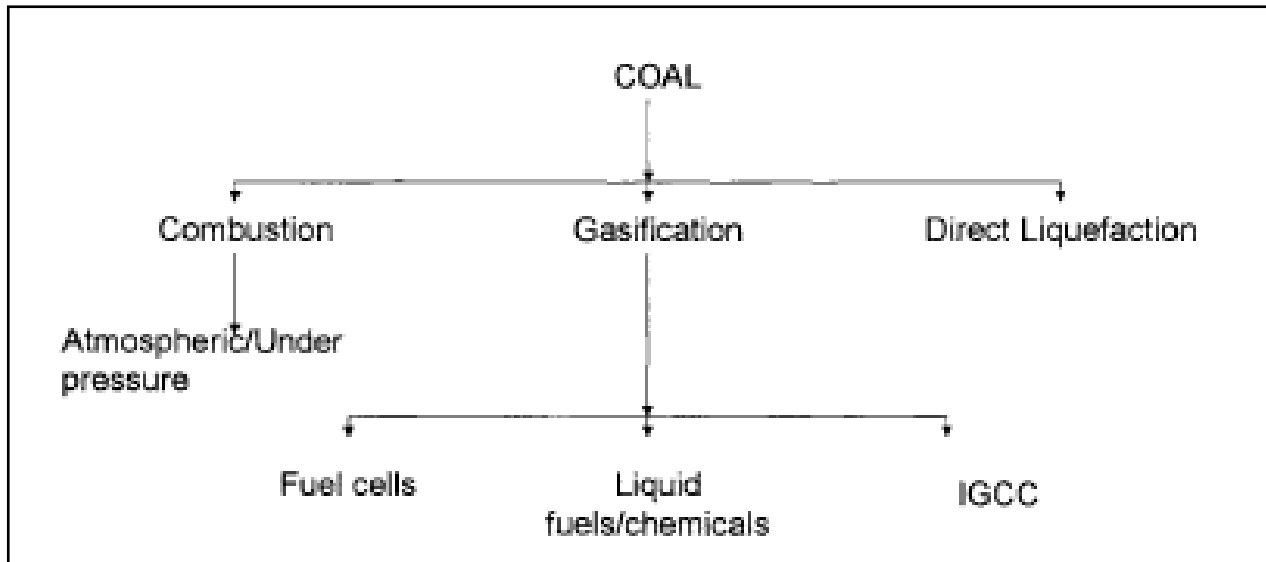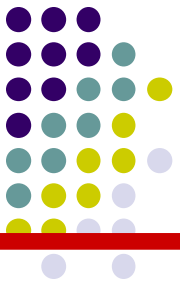| CV (kcal/kg)	%	Σ (%)
<1000	3.2	3.2
1001-2000	66.3	69.5
2001-3000	24.5	94.0
3001-4000	5.2	99.2
>4000	0.8	100

Alternative Solutions for more efficient & cleaner utilization of coal

Gasification?

➤ Gas fuels

➤ Liquid fuels

Gasification

Typical gas composition from gasification processes (T=550-2000°C, P 1-35 bar)

Gas	Composition(%)
CO	30 – 45
CO_2	5 – 25
H_2O	0 -12
H_2	20 – 35
H_2S	Up to 2

Sayed,et al., 2006.

Other impurities

❖ Particulates
❖ H_2S
❖ Tar
❖ NH_3
❖ HCl
❖ Alkaline vapors

Torres et al., 2007.

	Contaminant		
	Tars	H_2S	NH_3
Concentration range	1-150 mg/Nm^3	20-20.000	1.000-14.000

Problems
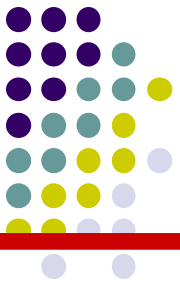
➢ Turkish lignites contains significant amount of sulfur.

➢ Based on location, the amount of sulfur in Turkish lignites ranges from 0.5% wt to 7.0% wt.

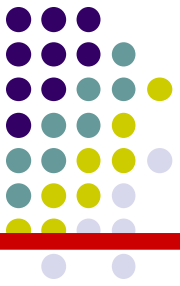➢ Nearly 50% of sulfur presented in the coal leaves the gasification system in the gas phase.

➢ Sulfur levels as high as 5000 - 10000 ppmv could be expected in the outlet stream of the gasifier.

Why sulfur removal ?

➢ Odor nuisance (an odor threshold of 0.5 ppb-2 ppb by volume),

➢ Inhalation of a single breath at a concentration of 1000 ppm (0.1%) may cause coma,

➢ Acceptable limits: 10 ppm (50 ppm for a duration of 10 minutes),

➢ Cause pipeline corrosion and limit plant lifetime,

➢ The sulfur limit (H_2S, COS, CS_2) for catalytic systems such as Fischer-Tropsch, methanol production or fuel cells: $\leq$ 1 ppmv

➢ For microturbines and gas engines, the limits for sulfur containing compounds are < 20 ppm, preferably <10 ppm
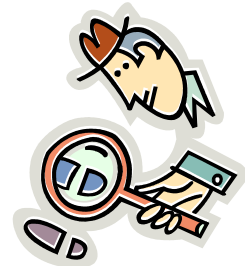
Conventiaonal Sulfur Removal
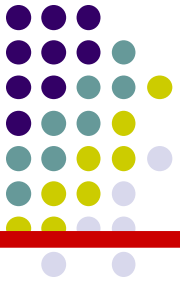
◈ In conventional treatment, H2S or other sulfur compounds are removed via low temperature amine scrubbers.

◈ Wastewater containing chemicals from the scrubbing process must be treated accordingly to prevent the contamination of drinking water.

◈ Removing H2S using scrubbers requires lowering the temperature of the syngas from 850°C (temperature of gasification) to 40-50°C with concurrent tar condensation.

◈ Tar condensation can cause plugging and fouling of the condenser and process piping. Tar build up on reactor walls makes the heat recovery inefficient.

◈ Tar is also a loss of hydrocarbon and leads to decrease in carbon utilization ratio.

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WILL WORK FOR CLEAN WATER

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High Temperature Sulfur Removal
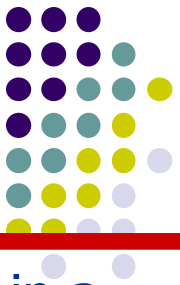
◇ RTI International estimated that desulfurization at 370-480°C in a 600 MW integrated gasification combined cycle (IGCC) plant could increase the overall process thermal efficiency by 3.6 efficiency points over conventional Selexol sulfur removal technology.

◇ This gain would reduce the plant cost by 269 USD per kW resulting in a associated 9.6% reduction of electricty cost.

◇ Considering that IGCC has a thermal efficiency of 40-50%, an increase of 3.6 thermal efficiency make sense

Dolomit
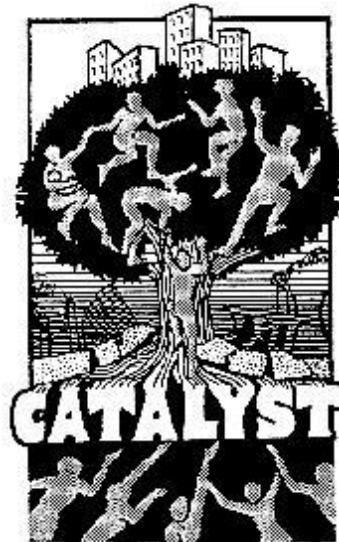
Why Tar Removal?
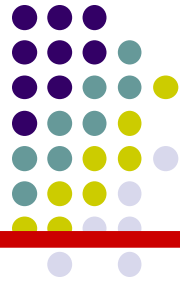
Among the byproducts of gasification, "tars" pose the greatest problem to end users. Upon condensation tars,

   block downstream pipelines
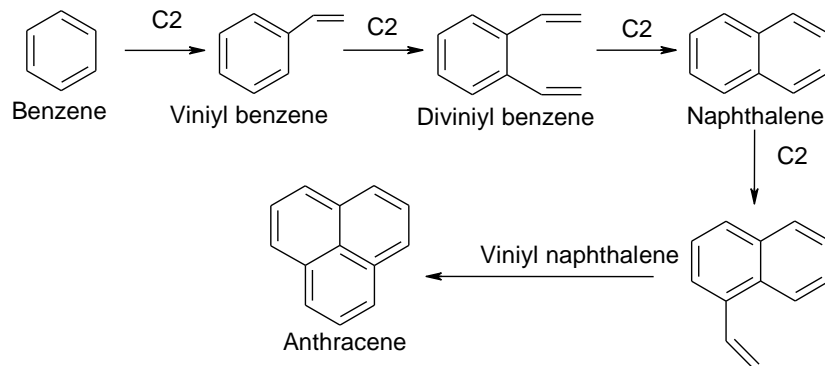   foul engines and turbines.
   Hinder heat transfer
   Poison catalysts.

Benzene $\xrightarrow{C2}$ Viniyl benzene $\xrightarrow{C2}$ Diviniyl benzene $\xrightarrow{C2}$ Naphthalene $\xrightarrow{C2}$ Viniyl naphthalene $\rightarrow$ Anthracene

Tar Removal Strategies

Phyisical Strategies (scrubber + filter)

- Not attractive because of their costs

- Maybe effective but liquid scrubbing produces large amounts of liquid waste / waste water requiring downstream treatment

- Reduced carbon efficiency

- Upon condensation, blocking of downstream pipelines and heat exchangers

- Environmental concerns for regulated emission products such as NOx and SO2

Catalytic Strategies

- more efficient

- improves the carbon efficiency

- Easy deactivation of the catalyst with the fouling, NH3 or H2S

Objective
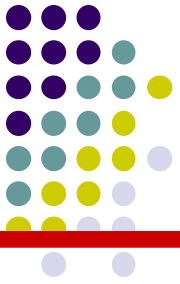
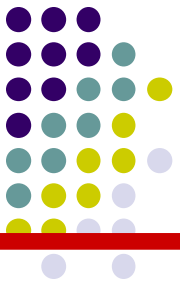In this study Preliminary results obtained from the hot gas cleanup research of an ongoing project "TRIJEN Liquid Fuel Production from Biomass and Coal Blends" on liquid fuels production from coal–biomass blends

Experimental-Sorbent

Sorbent:

Origin   : Eskisehir region
Particle size   : 2-3 mm
Amount   : 180 g

Chemical analysis of the dolomite used (wt %)

Moisture	Ignition loss	CaO	MgO	SiO_2	Fe_2O_3	Al_2O_3	MnO_4	Na_2O
0.010	45.980	36.930	16.880	0.081	0.098	0.125	0.003	0.050

Physical properties of the uncalcined and calcined dolomite

	BET (m^2/g)	Total Pore Volume (cc/g)	Average Pore Diameter (Å)
Uncalcined dolomite	0.069	0.00149	860.5
Calcined dolomite	11.3	0.2513	889.5

Experimental-Set Up
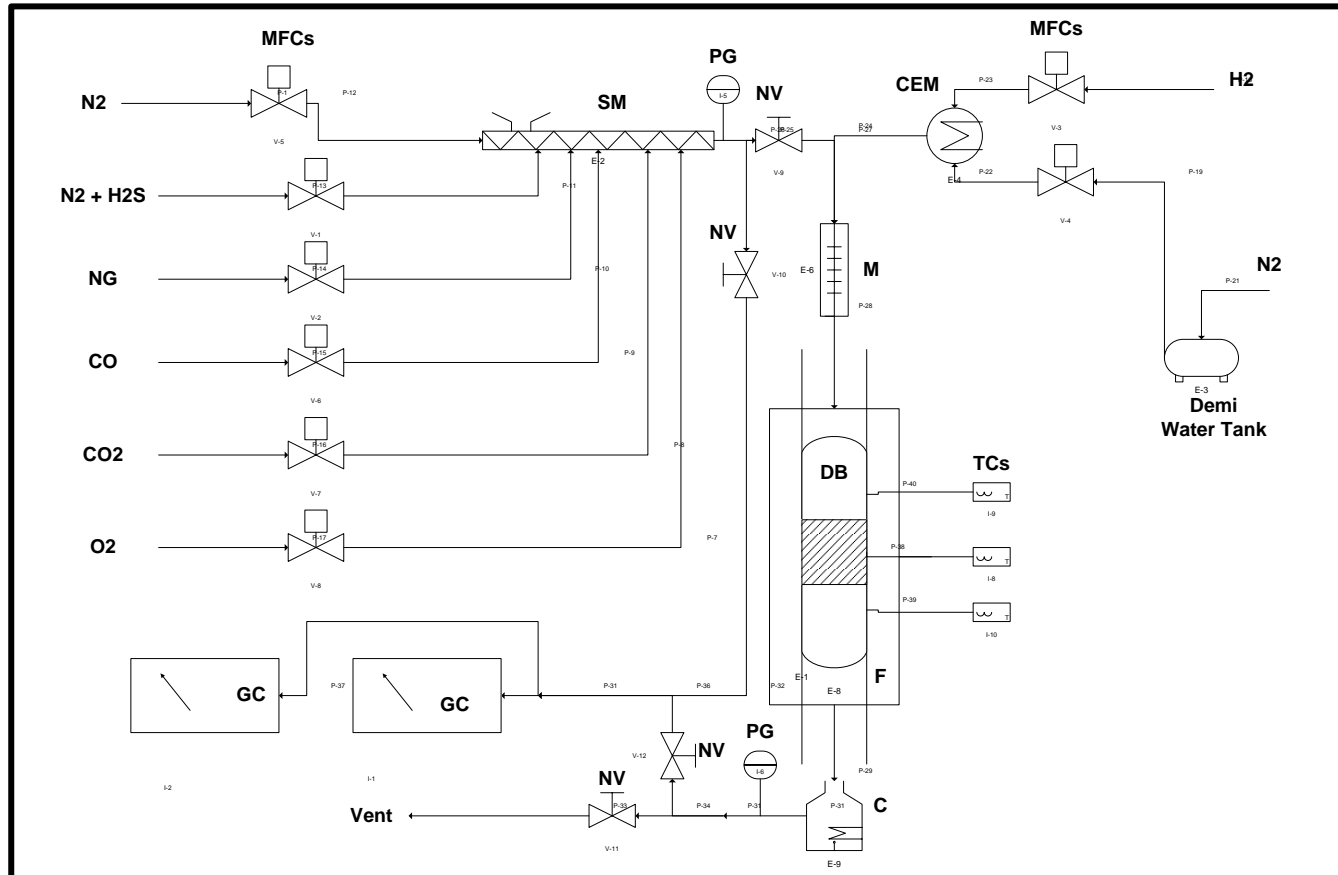
F: Furnace, **DB:** Dolomite fixed bed, **GC:** Gas Chromatography instruments for permanent gas and sulfur compound analysis, **MFC:** Mass flow control valves, **CEM:** Controlled evaporator and mixer, **M:** Mixing manifold, **NV:** Needle valve, **SM:** Static mixer, **PG:** Pressure gauge, **TC:** Thermocouple, C: Condenser

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Experimental-Set Up
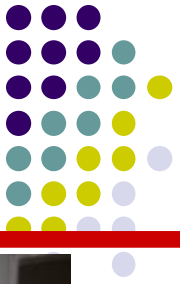
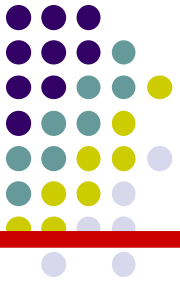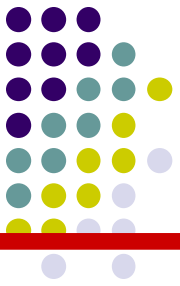# Results & Discusion

Removal of H_2S from binary, tertiary and simulated gasification outlet gas mixtures by dolomite.

Cases	Feed gas composition on wet Basis (v%)							Inlet H_2S concentration (ppmv, db*)	Outlet concentration of sulfur compounds (ppmv, db)		
	N_2	H_2	CO_2	CO	H_2O	CH_4	NG**	H_2S	H_2S	COS	CH_3SH
1	73	27	-	-	-	-	-	1460	~0	-	-
2	90	-	10	-	-	-	-	1800	2-3	-	-
3	90	-	-	10	-	-	-	1800	~0	1	-
4	64	26	10	-	-	-	-	1280	128	11	-
5	78.2	-	-	10.2	11.7	-	-	1564	157	9	-
6	85	-	10	-	-	-	5	1700	70	7	0.05
7	71.2	-	-	-	20.9	-	7.9	1424	190	-	0.01
8	8.5	54.6	3.0	13.7	15.1	5.1		200	140	11	-
9	63	27	7	-	-	-	3	1260	189	11	-

db: Dry basis, ** Natural gas is composed of 90% CH_4 + C2s-C5s, CO_2, N_2

- Cases 1-3   : Binary gas mixtures
- Cases 4-7   : Tertiary gas mixtures.
- Case 8   : Simulated mixture representing synthesis gases from a gasifier
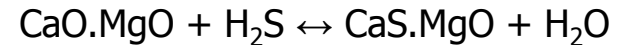- Case 9   : Gas mixtures contained NG.

H$_2$S Removal in N$_2$ Atmosphere:
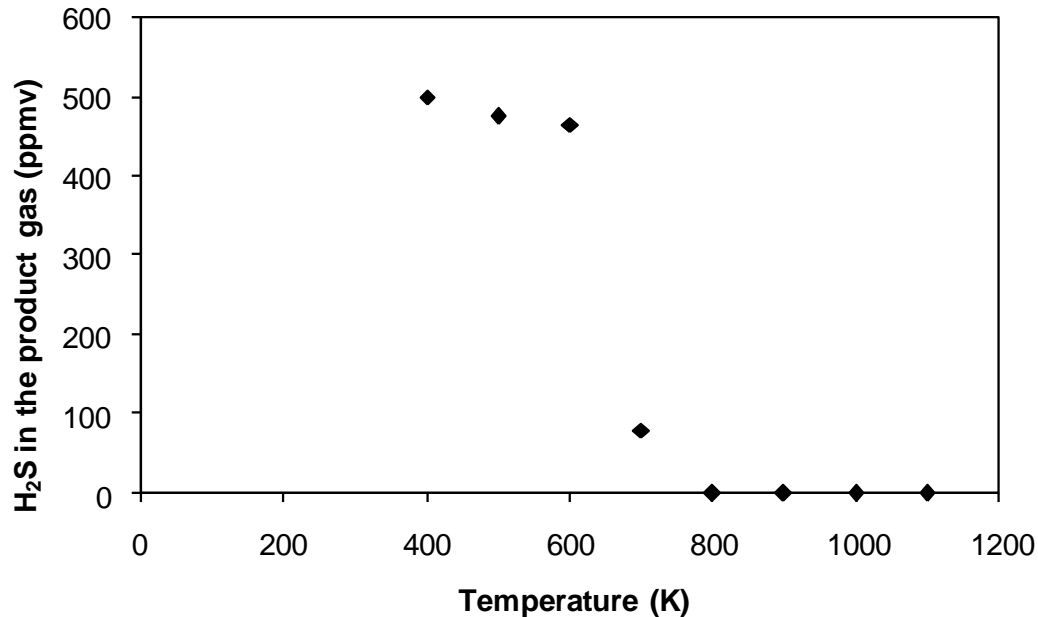
Change of H$_2$S amount in the product gas during H$_2$S removal by calcined dolomite with the temperature under pure N$_2$ atmosphere. P= 3 bar, GHSV = 5600 h^{-1}(at STP), C$_{H2S, inlet}$= 500 ppmv.

H$_2$S chemisorption on calcined &half-calcined dolomite

$$CaCO_3.MgO + H_2S \leftrightarrow CaS.MgO + CO_2 + H_2O$$

$$CaO.MgO + H_2S \leftrightarrow CaS.MgO + H_2O$$

At 700 K, the H$_2$S concentration in the reactor effluent gas was reduced to below 100 ppmv.
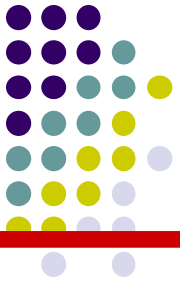
The degree of H$_2$S chemisorption on dolomite reached to a maximum level at around 773 K.

The H$_2$S levels of the effluent gases below 1 ppmv were observed between 773 and 1073 K.
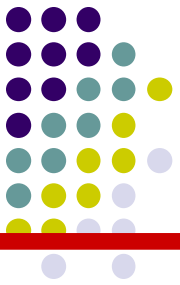
TD Prediction: The H$_2$S concentration in the equilibrium at 750 K is around 0.16 ppmv.
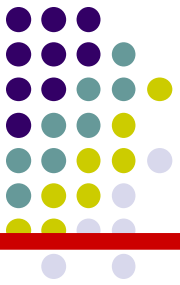
H_2S Removal from Binary Gas Mixtures Using Dolomite

H$_2$S Removal from Binary Gas Mixtures Using Dolomite

Case 1:

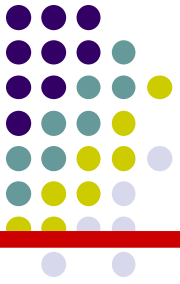| Cases	Feed gas composition on wet Basis (v%)							Inlet H$_2$S concentration (ppmv, db*)	Outlet concentration of sulfur compounds (ppmv, db)		
	N$_2$	H$_2$	CO$_2$	CO	H$_2$O	CH$_4$	NG**	H$_2$S	H$_2$S	COS	CH$_3$SH
1	73	27	-	-	-	-	-	1460	~0	-	-

- All H$_2$S was captured by dolomite
- The composition of the reactor effluent gas did not change indicating that no other reaction took place in addition to the chemisorption of the H$_2$S.
- H$_2$ behaved like an inert gas and, consequently the results obtained from H$_2$S removal process with H$_2$-N$_2$ mixture have been similar to that obtained with H$_2$S in the pure nitrogen.

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Case 2:

Cases	Feed gas composition on wet Basis (v%)							Inlet H_2S concentration (ppmv, db*)	Outlet concentration of sulfur compounds (ppmv, db)		
	N_2	H_2	CO_2	CO	H_2O	CH_4	NG**	H_2S	H_2S	COS	CH_3SH
1	73	27	-	-	-	-	-	1460	~0	-	-
2	90	-	10	-		-	-	1800	2-3	-	-

- Dolomite was still very effective: reducing the H_2S level from 1800 ppmv to around 3 ppmv.

- The equilibrium H_2S concentration under these conditions was calculated to be ~1.3 ppmv.

- No change was observed in the composition of inlet gas indicating that there was no other reactions occurred.
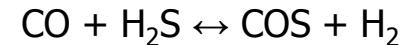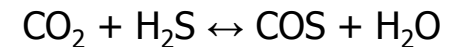
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Case 3:

Cases	Feed gas composition on wet Basis (v%)							Inlet H_2S concentration (ppmv, db*)	Outlet concentration of sulfur compounds (ppmv, db)		
	N_2	H_2	CO_2	CO	H_2O	CH_4	NG**	H_2S	H_2S	COS	CH_3SH
3	90	-	-	10	-	-	-	1800	~0	1	-

- The inlet gas composition changed during the experiment.
- The CO concentration decreased from 10 v% to 7.7 v% while 1.6 v % CO_2 was measured in the reactor effluent gas stream.
- CO_2 existence in effluent gas indicated that the Boudouard reaction, which is taking place according the following reaction, can be likely responsible for CO_2 formation.
- A trace amount of COS formed while no H_2S was detected in the reactor effluent gas. COS was reported to form in the existence of CO and or CO_2 due to the reactions between these components and H_2S through the following reactions

Boudouard: $2CO \leftrightarrow CO_2 + C$

COS formation:

$CO_2 + H_2S \leftrightarrow COS + H_2O$
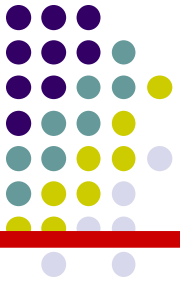
$CO + H_2S \leftrightarrow COS + H_2$

The formation of COS is severely temperature limited and inhibited by hydrogen.

Under the experimented conditions of this study, it was more probable that COS was formed due the presence of CO as no COS was detected during the experiment done with 10 vol % CO_2 in N_2.
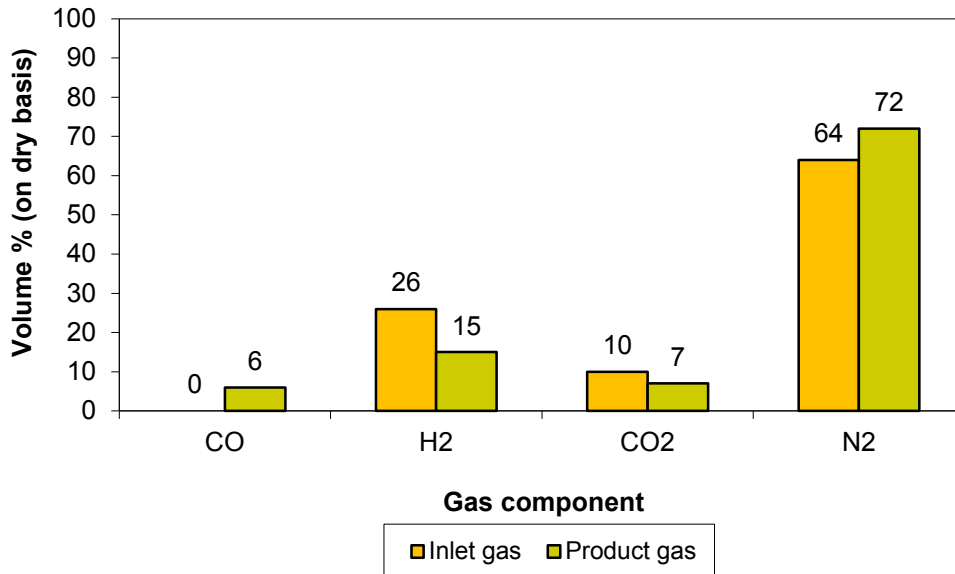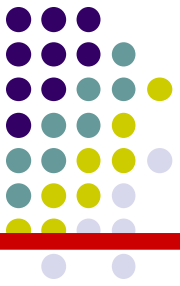
Results & Discussion
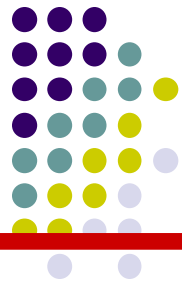
H$_2$S Removal from Tertiary Gas Mixtures Using Dolomite

Case 4:

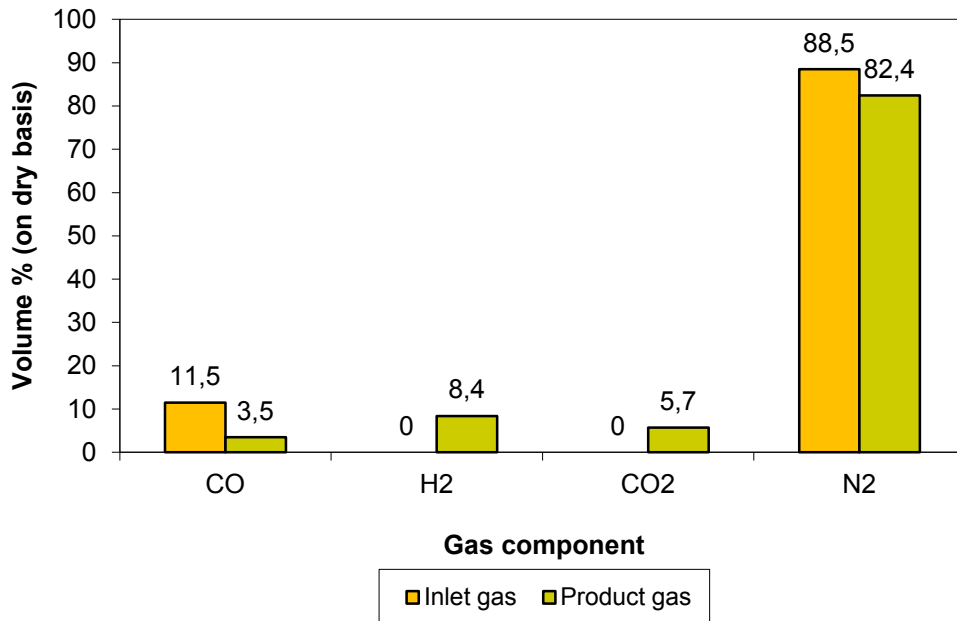| Cases	Feed gas composition on wet Basis (v%)							Inlet H_2S concentration (ppmv, db*)	Outlet concentration of sulfur compounds (ppmv, db)		
	N_2	H_2	CO_2	CO	H_2O	CH_4	NG**	H_2S	H_2S	COS	CH_3SH
4	64	26	10	-	-	-	-	1280	128	11	-

Changes in the gas composition during the H_2S removal by calcined dolomite in Case 4. Dry basis, T = 1023 K, P = 3 bar, GHSV = 5600 h^{-1} (at STP), $C_{H2S, inlet}$= 1280 ppmv.

- About 90 % of H_2S removed
- However, H_2S in the reactor effluent gas stream measured as ~128 ppm higher than the equilibrium H_2S concentration of 50 ppm predicted by TD calculation.
- H_2S removal efficiency was lower than that obtained with the binary gas mixtures
- This might be attributed to the existence of CO_2 in the reactants and the water vapor produced as result of WGS reaction. The water vapor reduces the activity of dolomite toward H_2S. This tertiary gas seemed to promote the formation of COS to a larger extend in comparison to the binary mixture with similar CO

Case 5:

Cases	Feed gas composition on wet Basis (v%)							Inlet H_2S concentration (ppmv, db*)	Outlet concentration of sulfur compounds (ppmv, db)		
	N_2	H_2	CO_2	CO	H_2O	CH_4	NG**	H_2S	H_2S	COS	CH_3SH
5	78.2	-	-	10.2	11.7	-	-	1564	157	9	-

- The possibility of WGS reaction was investigated.
- H_2S removal effeciency : ~ 90%
- 9 ppm COS was observed
- Gas composition changed considerably resulting in 5.7 vol % CO_2 and 8.4 vol % H_2 in the product gas,
- This was indicated that the gas atmosphere with water vapor enhanced the WGS reaction on the dolomite surface. Consequently, as it might be expected, the carbon monoxide concentration decreased from 11.5 vol % to 3.5 vol% on a dry basis.

Changes in the gas composition during the H_2S removal by calcined dolomite in Case 5. Dry basis, T = 1023 K, P = 3 bar, GHSV = 5600 h^{-1} (at STP), $C_{H2S, inlet}$= 1564 ppmv.
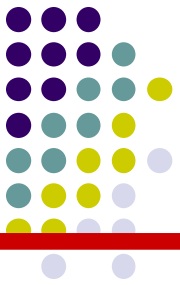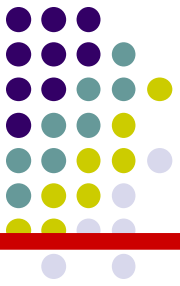
These two cases (case 4 and 5) showed that :

The water gas shift (WGS) and the reverse water gas shift (RWGS) reactions could occurred during the hot gas desulfurization by dolomite.

Direction of the reactions, however, was dictated by the gas composition where the thermodynamic equilibrium was attained.
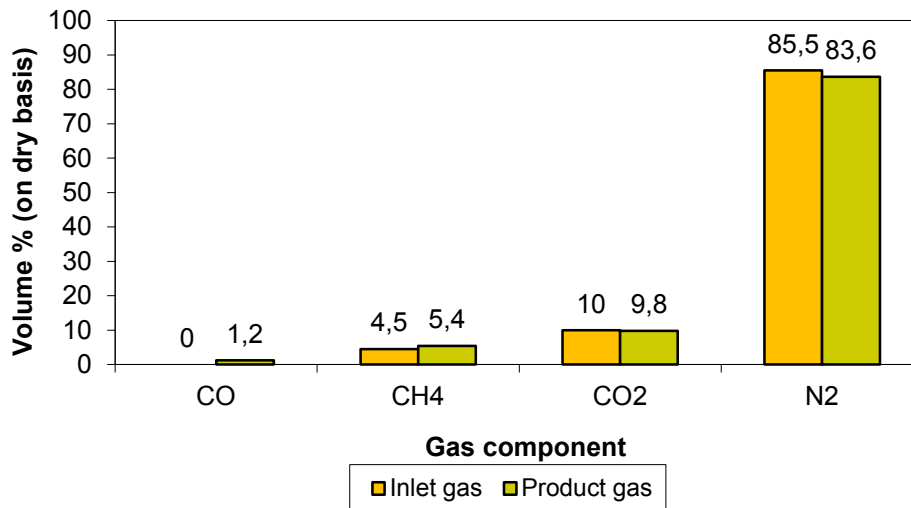
The thermodynamic equilibrium conversion of CO to CO_2 via the water gas shift reaction at 1023 K was calculated as ~% 53 according to the thermodynamic equilibrium correlation given below [16]:
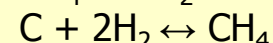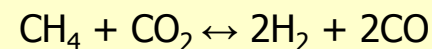
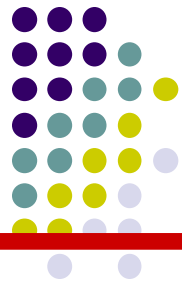$$Log(K) = -2.4198 + 0.000385T + \frac{2180.6}{T}$$

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Results & Discussion

Case 6: Simulating dry reforming

Cases	Feed gas composition on wet Basis (v%)							Inlet H_2S concentration (ppmv, db*)	Outlet concentration of sulfur compounds (ppmv, db)		
	N_2	H_2	CO_2	CO	H_2O	CH_4	NG**	H_2S	H_2S	COS	CH_3SH
6	85	-	10	-	-	-	5	1700	70	7	0.05

Changes in the gas composition during the H_2S removal by calcined dolomite in Case 6. Dry basis, T = 1023 K, P = 3 bar, GHSV = 5600 h^{-1} (at STP), $C_{H2S, inlet}$ = 1700 ppmvv.
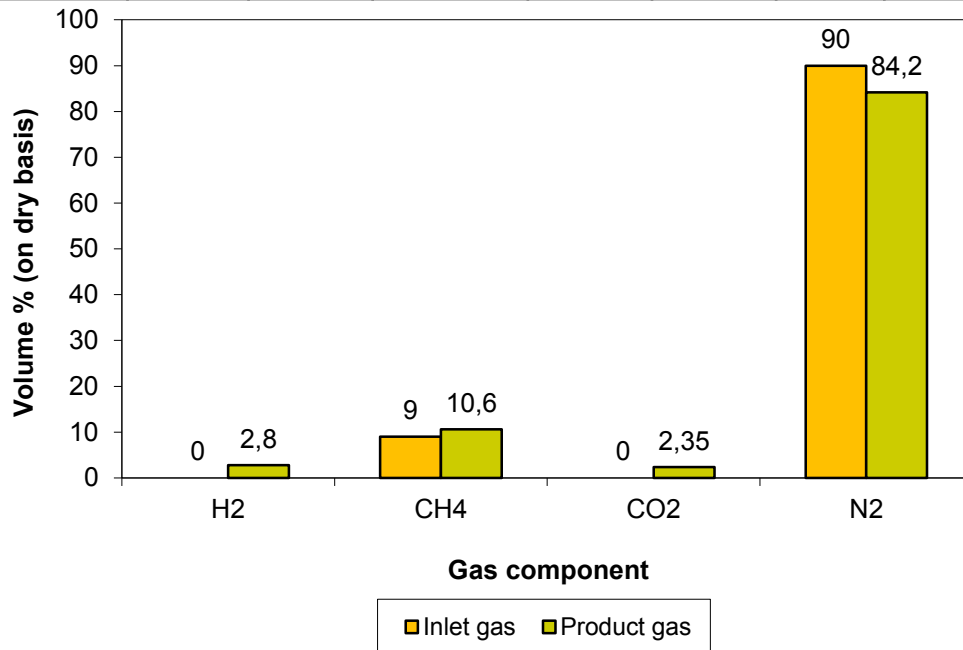
- Aim: To investigate the possibility of the occurrence of this reaction
- About 95 % of H_2S removed
- 1.2 vol % CO was detected in the product gas while the amount of methane slightly increased from 4.5v% to 5.4v%.
- No H2 was observed in the outlet stream, suggesting that either the dry reforming reaction (reaction 10) did not occur at all or H2 was consumed immediately after its formation as an intermediate product by any possible reaction such as hydrogenation of carbon deposited on the dolomite surface (reaction 11).
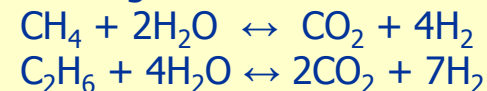
$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO$
$C + 2H_2 \leftrightarrow CH_4$

Case 7: Simulating steam reforming

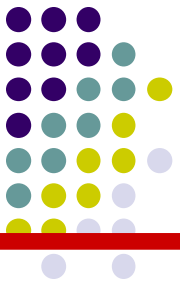| Cases	Feed gas composition on wet Basis (v%)							Inlet H$_2$S concentration (ppmv, db*)	Outlet concentration of sulfur compounds (ppmv, db)		
	N$_2$	H$_2$	CO$_2$	CO	H$_2$O	CH$_4$	NG**	H$_2$S	H$_2$S	COS	CH$_3$SH
7	71.2	-	-	-	20.9	-	7.9	1424	190	-	0.01

Changes in the gas composition during the H$_2$S removal by calcined dolomite in Case 7. Dry basis, T = 1023 K, P = 3 bar, GHSV = 5600 h^{-1} (at STP), C$_{H2S,\ inlet}$= 1424 ppmv

- About 86% of H$_2$S removed
- No COS and CO was detected in the product gas. These results supported the findings that the existence of CO favors COS formation.
- Although in a conventional steam methane reforming reaction, CO and H$_2$ were expected to form as products, in these experiments no CO was observed. Instead, CO$_2$ formed along with H$_2$. This might be attributed to the excess of steam. Surplus steam might be the reason of CO$_2$ formation instead of CO according to the following reactions:
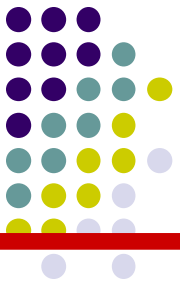
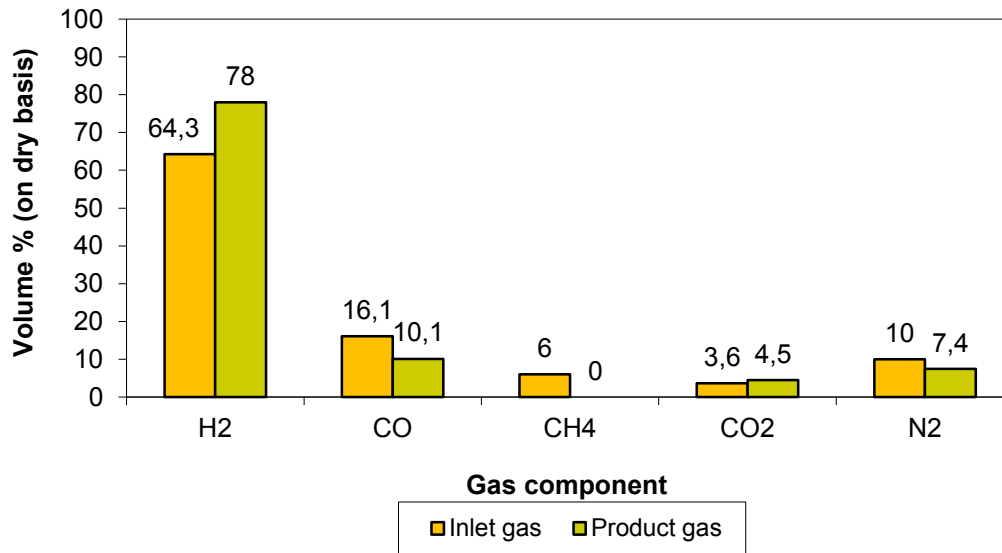$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$$
$$C_2H_6 + 4H_2O \leftrightarrow 2CO_2 + 7H_2$$

Results & Discussion

H$_2$S Removal from Simulated Gasifier Outlet Gas Mixtures: The effect of H$_2$S load
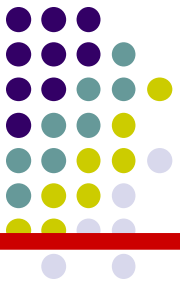
Case 8:Simulatig gasifier outlet

Cases	Feed gas composition on wet Basis (v%)							Inlet H_2S concentration (ppmv, db*)	Outlet concentration of sulfur compounds (ppmv, db)		
	N_2	H_2	CO_2	CO	H_2O	CH_4	NG**	H_2S	H_2S	COS	CH_3SH
8	8.5	54.6	3.0	13.7	15.1	5.1		200	140	11	-

Changes in the gas composition during the H_2S removal by calcined dolomite in Case 8. Dry basis, T = 1023 K, P = 3 bar, GHSV = 5600 h^{-1} (at STP), $C_{H2S, inlet}$= 200 ppmv.
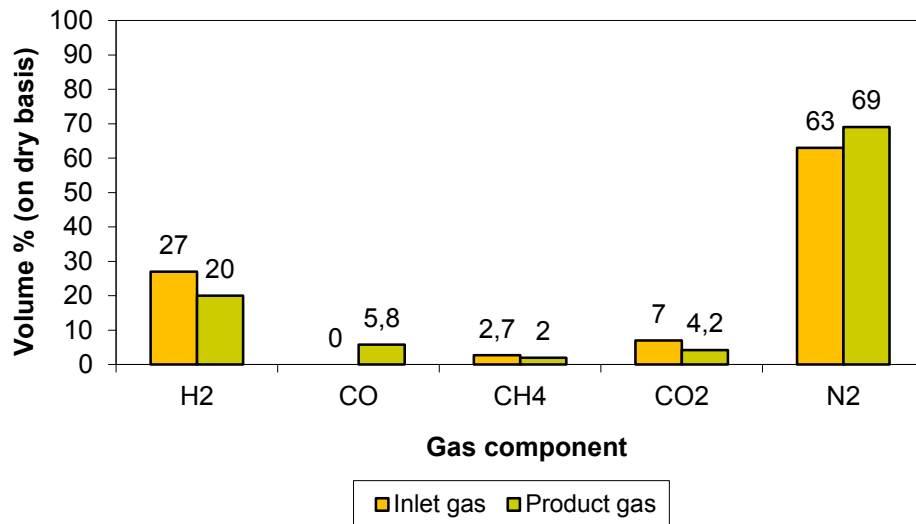
- H_2S removal is obviously low. Efficiency: 30 %

- Thermodynamic calculations with this inlet gas composition dictated a maximum achievable equilibrium H_2S of ~120 ppm. Hence a 140 ppmv in the reactor off gas seems to be reasonable.

- The changes in the outlet gas stream with increased H_2 and decreased CO, indicated that the WGS reaction also took place to some extent.
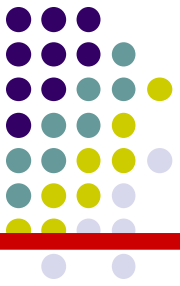- The carbonyl sulfur formed likely due to the reaction between H_2S and CO/CO_2.

Case 9:

Cases	Feed gas composition on wet Basis (v%)							Inlet H_2S concentration (ppmv, db*)	Outlet concentration of sulfur compounds (ppmv, db)		
	N_2	H_2	CO_2	CO	H_2O	CH_4	NG**	H_2S	H_2S	COS	CH_3SH
9	63	27	7	-	-	-	3	1260	189	11	-

- H_2S Removal efficiency: ~ of 85 %,

- Apparently the reverse water gas shift reaction ($CO_2 + H_2 \leftrightarrow CO + H_2O$) occurred in the reactor resulting in a decrease in H_2 and CO_2 percentages and producing CO and water vapor which was not existed in the inlet gas stream.

Changes in the gas composition during the H_2S removal by calcined dolomite in Case 9. Dry basis, T = 1023 K, P = 3 bar, GHSV = 5600 h^{-1} (at STP), $C_{H2S, inlet}$= 1260 ppmv.

Results & Discussion

The results of these studies showed that:

◈ H_2S removal by dolomite is limited to around 150-200 ppmv.

◈ Due to thermodynamical constraints, the H_2S removal efficiencies with calcium containing materials are only on the order of 90 % under typical gasification conditions, resulting in residual H_2S levels of 100 ppmv or greater.

◈ This may suggest that dolomite could be used for strictly bulk H_2S removal requiring an additional bed to further polish the gas for the applications with more stringent sulfur cleanup.

Results & Discussion
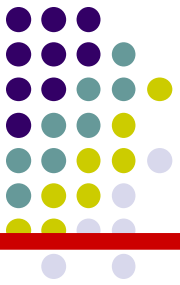
Tar removal by dolomite (Preliminary results)

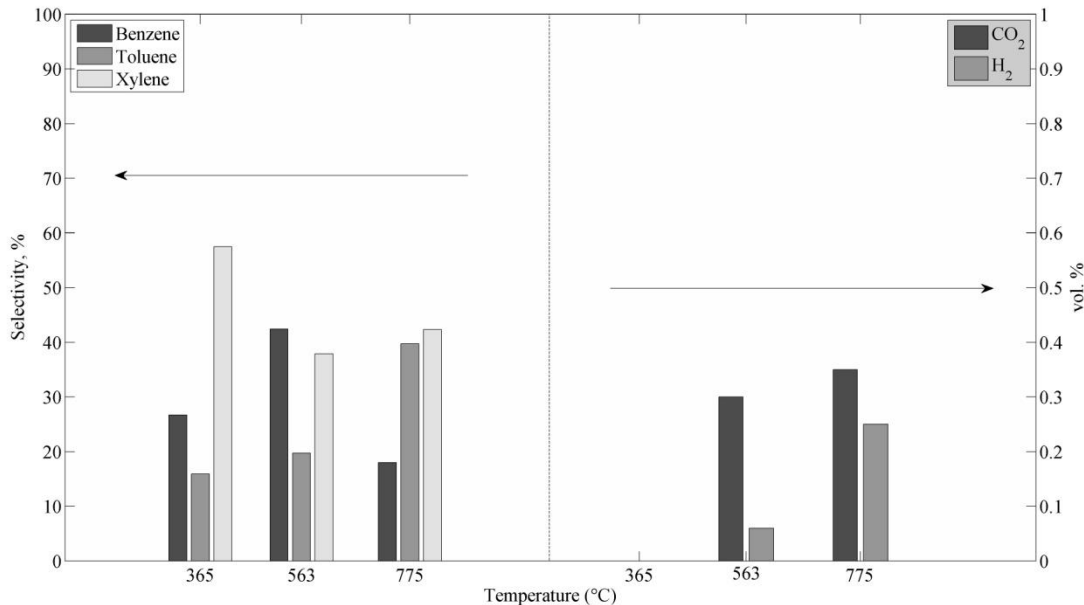| Experimental conditions	Feed gas composition, %V (db)	Outlet gas composition, %V(db)	Contaminants, inlet	Contaminant, outlet
T_r=750°C Steam/C=0.21 Steam/tar=4.9	% 28.5 CO, % 25.0 CO_2, % 31.4 H_2, % 3.2 CH_4, % 11.9 N_2	% 35 CO, % 22.0 CO_2, % 25 H_2, % 4.0 CH_4, % 14.0 N_2	240 ppmv H_2S 8.67 gC/Nm³ 2.63 g C/Nm³ Benzene 2.60 g C/Nm³ Toluene 3.44 g C/Nm³ Xylene	216 ppmv H_2S with trace COS 7.28 gC/Nm³ 4.62 g C/Nm³ Benzene 2.28 g C/Nm³ Toluene 0.38 g C/Nm³ Xylene

- Dolomite showed a low degree of tar removal activity.

- Xylene and toluene concentrations decreased whereas benzene concentration increased in the outlet stream.

- At 750°C thermally/catalytically broken methyl groups in toluene producing benzene and methane.

- With the same mechanism, xylene was dealkylated into toluene and benzene, consecutively in the presence of exces hydrogen. The increase in methane percentage from 3.2% to 4.0% supported this suggestion.
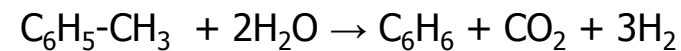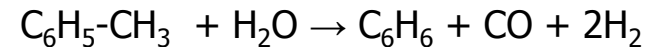
Sarioglan(2012)

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Results & Discussion

Tar removal by comercial catalyst

(Catalyst: Precios metal based, monoliths with L = 25.4 mm and R = 20 mm)

The change of tar compound selectivity and formation of gasous products with reaction temperature on commercial precious metal based steam reforming catalyst under nitrogen atmosphere. 3.82 Nl/min N_2, 15.45 g/h Xylene, 5.5 g/h H_2O and GHSV of ~22500 h^{-1}, Steam/C=0.26, Steam/Xylene=2.1

- Xylene was converted into benzene and toluene.

- Gases such as CO, CO2, H_2, CH4 were detected at 563°C.

- This proces can be attributed to steam dealkylation reactions according to the reaction mechanisms .
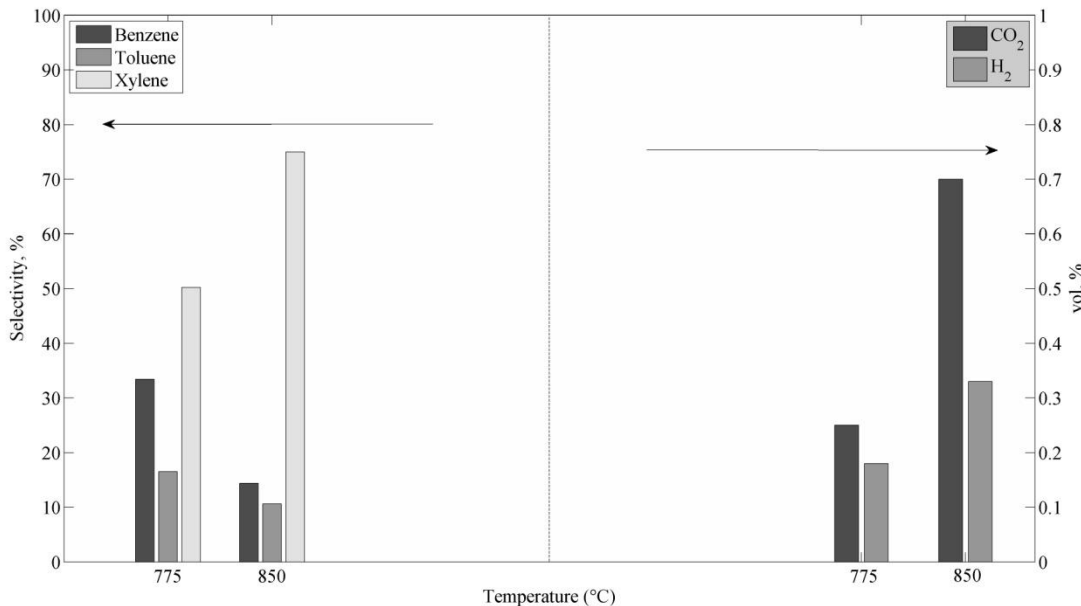
- At 775°C: tar reduced from 61gC/Nm^3 to 6.6 gC/Nm^3

$$C_6H_5\text{-}CH_3 + H_2O \rightarrow C_6H_6 + CO + 2H_2$$

$$C_6H_5\text{-}CH_3 + 2H_2O \rightarrow C_6H_6 + CO_2 + 3H_2$$

Sarioglan(2012)

Tar removal by comercial catalyst

H2 and CO2 formation percentages and benzene, toluene and xylene selectivities in nitrogen stream at the outlet at two different reaction temperatures with similar inlet xylene loads of around 28 g C/Nm3 under nitrogen atmosphere with a GHSV of 22500 h-1

At high temperature (850oC):

- 97.3% of tar has been removed. In

- More xylene was left in remained outlet tar stream at 850°C , due to coking of aromatic compounds via polymerization or degradation might be the prevailing reaction instead of steam dealkylation with increasing the operation temperature.

- Presence of H2 and CO2 might be taken as a measure of slight increases in steam reforming activity of the catalyst
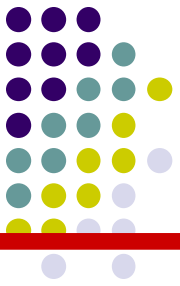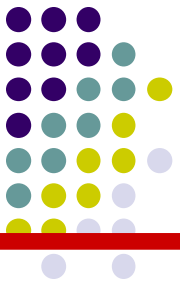
Tar removal by comercial catalyst
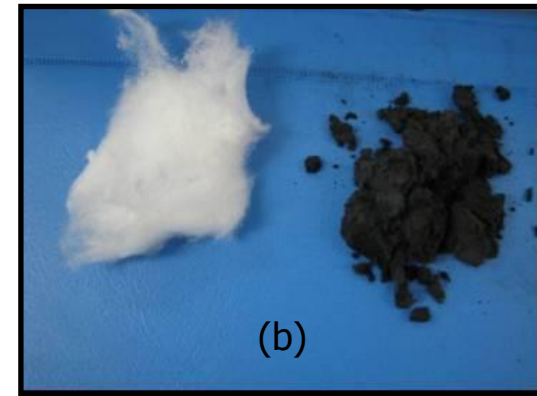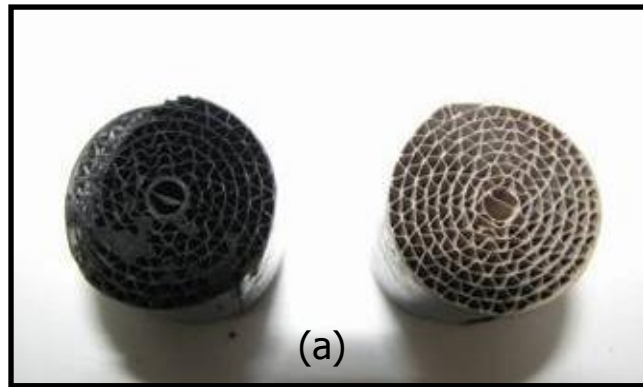
Carbon deposition on the (a) the fresh (right) and used (left) catalyst, (b) Fresh (left) and used (right) glass wool supporting catalyst bed

Conclusions

H2S removal performance of dolomite is strongli depens on operating temperature. Operating temperature need to be higher than 700K.
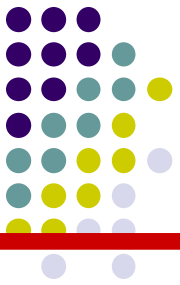
Removal degree of H_2S from hot gases by dolomite dictated by thermodynamic limitations

During H2S removal process, in addition to H_2S chemisorption, the WGS and RWGS reactions may occur depending on gas composition.

The Boudouard reaction was another concern to be taken into account.

Conclusions

Deactivation of CaO likely occurred at high CO_2 concentrations in the atmosphere, namely higher than 10 % by volume at ~ 1023 K.

COS formed during the H_2S removal by dolomite, possibly due to the presence of CO. Higher H_2S levels in the gas stream could likely improve the kinetics of reactions between CO/CO_2 and H_2S which produce COS.

Preliminary results showed that dolomite has some activity toward Tar (benzene, toluene and xylene as surrogated compounds).
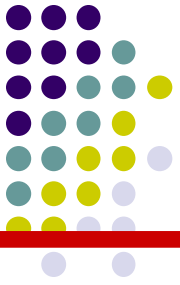
The comercil precious metal based catalyst catalyst catalyzes dealkylation reaction tar components such as xylene

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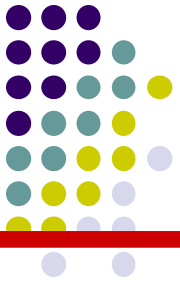
THANK YOU

THANK YOU VERY MUCH FOR YOUR KIND ATTENTION

Torres, w, Pansare s. s, and Goodwin, j. G., Hot Gas Removal of Tars, Ammonia, and Hydrogen Sulfide from Biomass Gasification Gas, Catalysis Reviews, 49:407–456, 2007.

Sarıoğlan, A., Tar Removal on Dolomite and Steam Reforming Catalyst: Benzene, Toluene and Xylene Reforming, International Journal of hydrogen energy (in press).