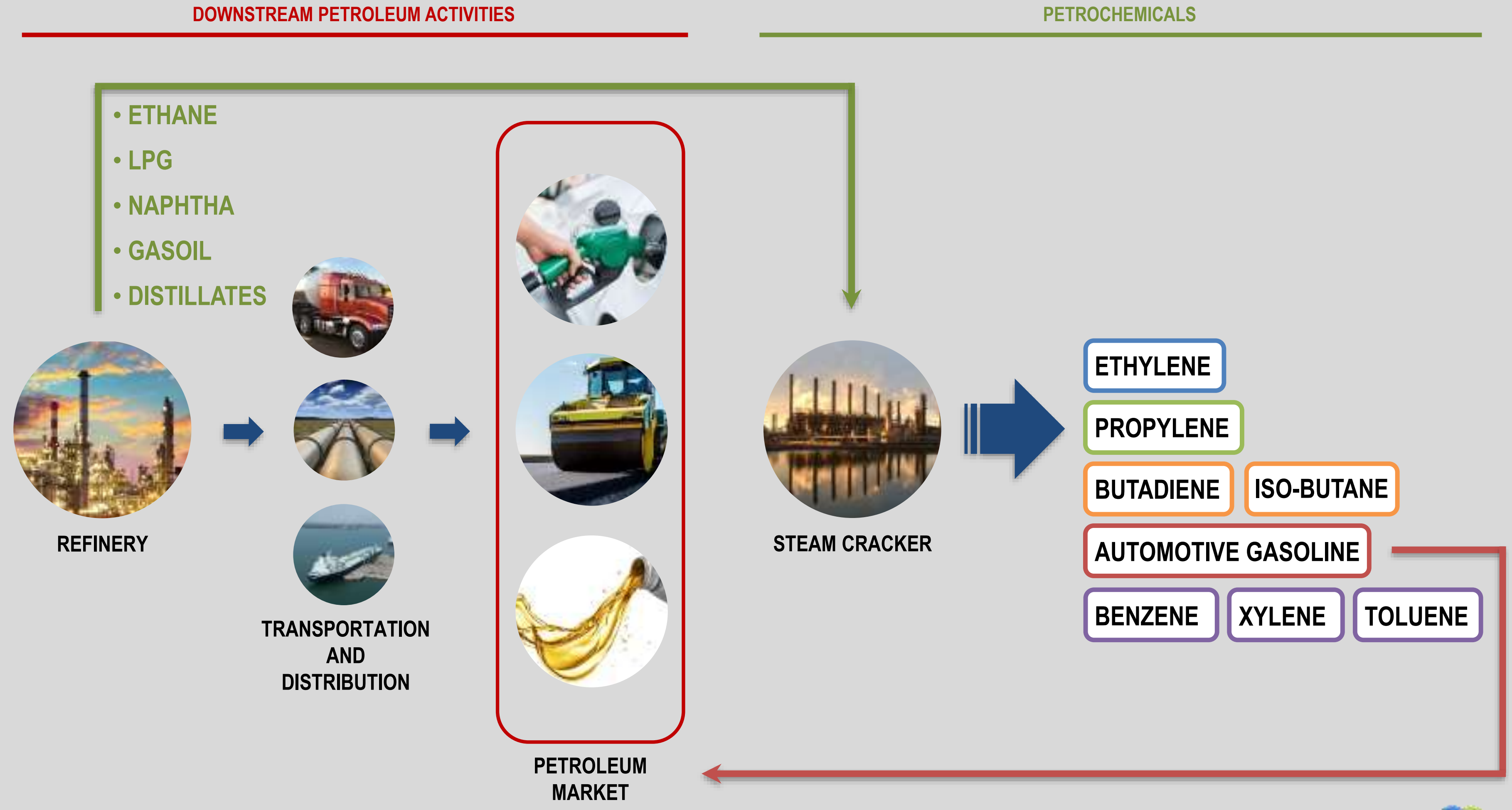
STEAM CRACKING

STEAM CRACKERS :

LOCATION, FEEDSTOCKS AND PRODUCTS


DOWNSTREAM PETROLEUM ACTIVITIES
PETROCHEMICALS
• ETHANE
• LPG
• NAPHTHA
• GASOIL
• DISTILLATES
REFINERY
TRANSPORTATION
AND
DISTRIBUTION
PETROLEUM
MARKET
STEAM CRACKER
ETHYLENE
PROPYLENE
BUTADIENE
ISO-BUTANE
AUTOMOTIVE GASOLINE
BENZENE
XYLENE
TOLUENE

PONA

PARAFFINS, OLEFINS, NAPHTHENES & AROMATICS

WHAT YOU NEED TO KNOW ABOUT ORGANIC CHEMISTRY

SATURATED HYDROCARBONS

SINGLE “C-C” BOND

- **CHAINS**
  - PARAFFINS
    - N-PARAFFINS
    - ISO-PARAFFINS
- **CYCLES**
  - NAPHTHENES
    - CYCLO-PARAFFINS

UNSATURATED HYDROCARBONS

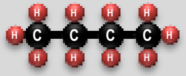
DOUBLE “C-C” BONDS

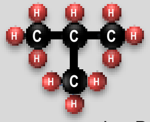
- **BENZENIC CYCLES**
  - AROMATICS
- **CHAINS**
  - OLEFINS (1 x C=C)
  - DIOLEFINS (2 x C=C)

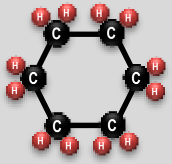
TRIPLE “C-C” BONDS

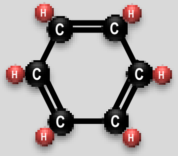
- **CHAINS**
  - ACETYLENICS

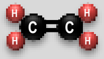
Examples

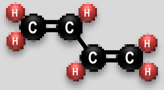

n-Butane

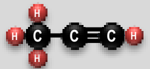

iso-Butane


Cyclohexane


Benzene


Ethylene


1,3-Butadiene


Propyne

STABLE HC (saturated hydrocarbons)

VERY REACTIVE HC (unsaturated hydrocarbons)

A LITTLE HISTORY

ABOUT STEAM CRACKING

1920 1942 1950 1960 TODAY

Naphtha steam crackers : 1MT/year of ethylene

Naphtha steam crackers : 300kT/year of ethylene

Construction of units with a capacity up to 50kT/year of ethylene

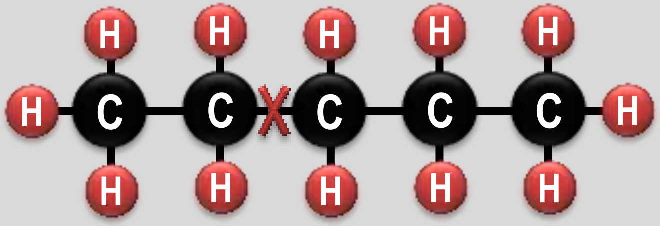
Diesel fuel steam cracking : 6kT/year of ethylene

Ethylene from cracking ethane

CRACKING CONDITIONS

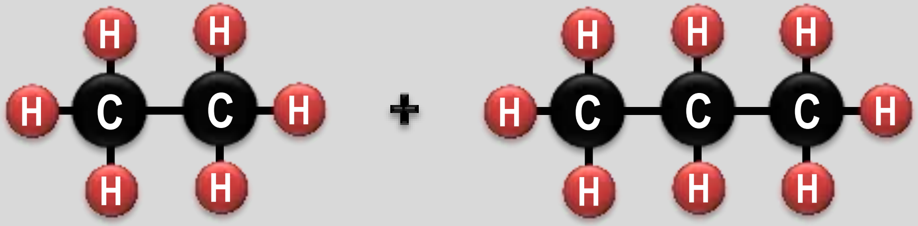
CRACKING CONDITIONS

PENTANE C_5H_{12}



CRACKING C–C BONDS

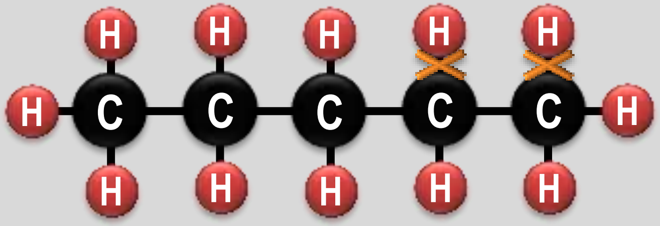
ETHANE C_2H_6



PROPANE C_3H_8

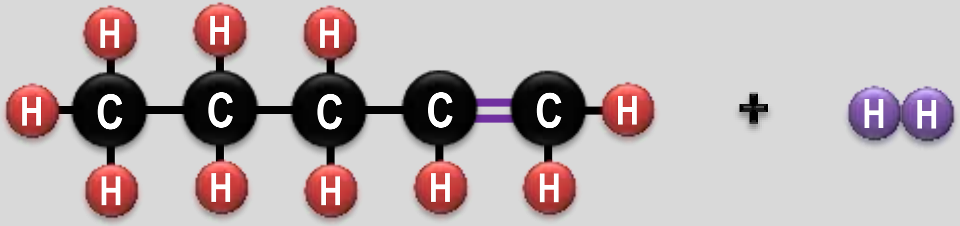
CRACKING CONDITIONS

PENTANE C_5H_{12}



CRACKING C–H BONDS

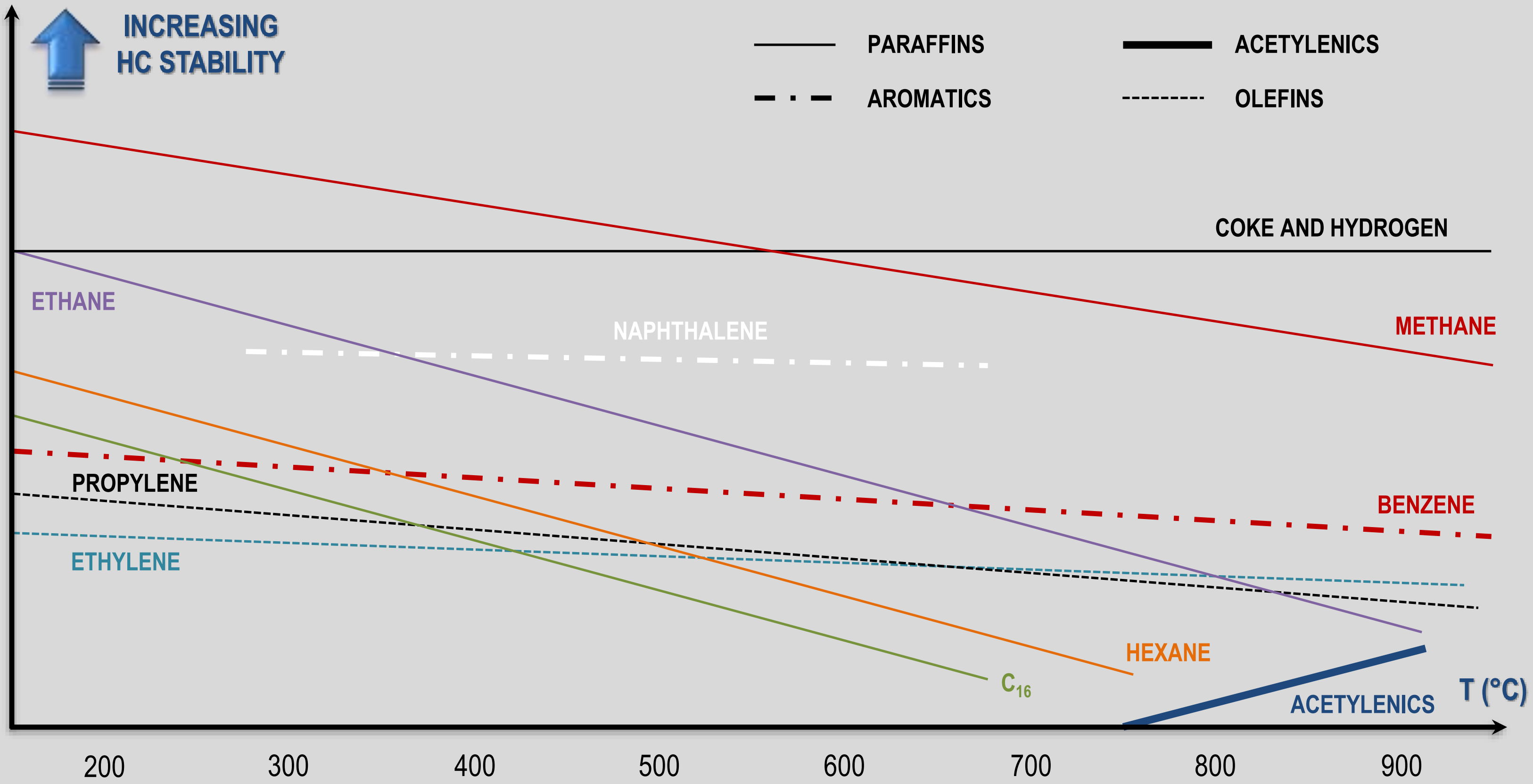
PENTENE C_5H_{10}

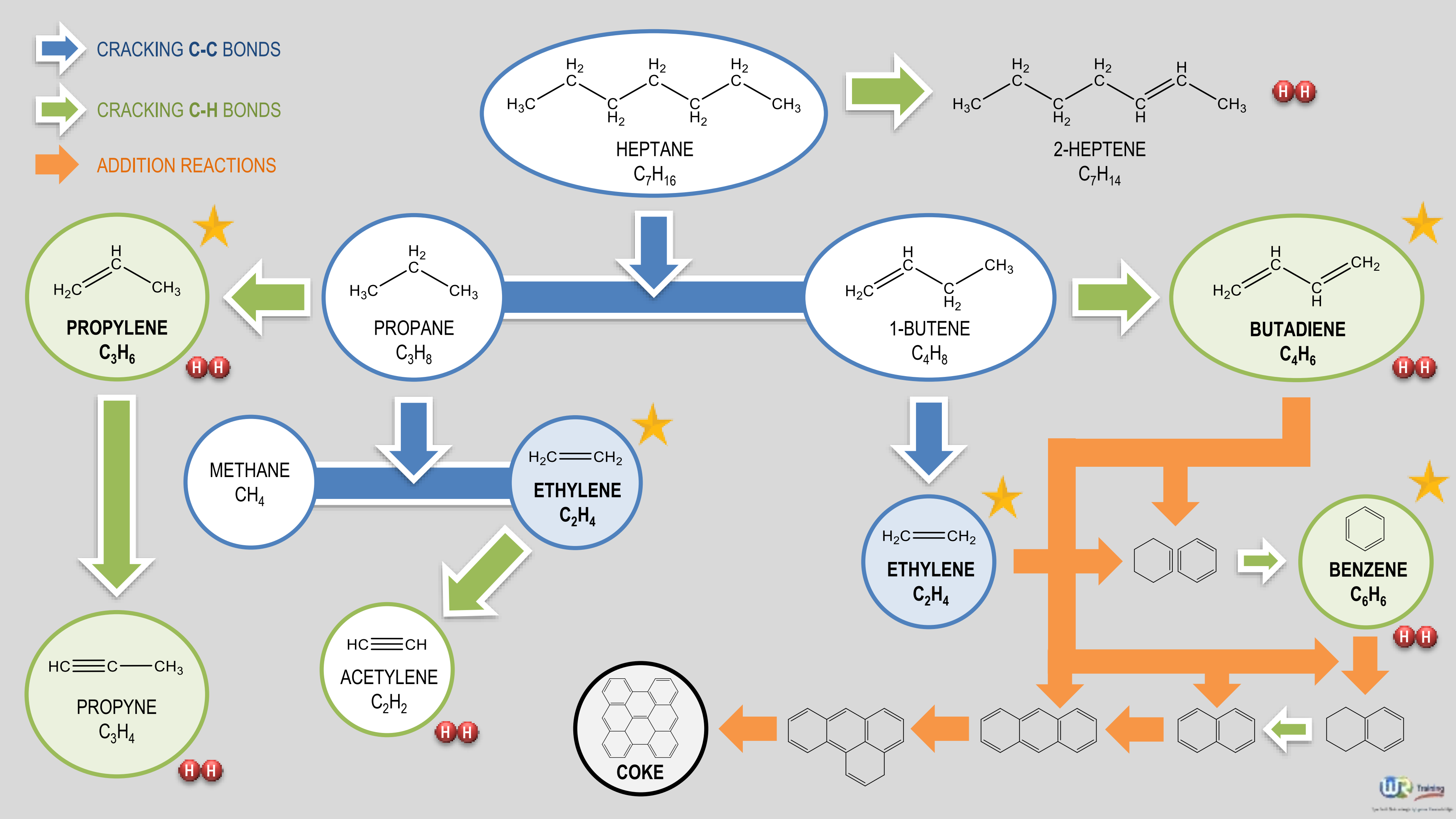


HYDROGEN H_2

CRACKING CONDITIONS

- Steam cracking requires **extreme** process conditions :
  - Cracking temperature : 800 – 850°C
  - Residence time : 0.1 – 0.5 sec
  - Cracking pressure : slightly higher than atmospheric pressure
  - Dilution of the feed with large quantities of steam : ~0.6 T of steam per 1 T of naphtha feed


INCREASING
HC STABILITY
PARAFFINS
ACETYLENICS
AROMATICS
OLEFINS
COKE AND HYDROGEN
ETHANE
NAPHTHALENE
METHANE
PROPYLENE
BENZENE
ETHYLENE
HEXANE
C_{16}
ACETYLENICS
T (°C)
200
300
400
500
600
700
800
900



CRACKING C-C BONDS
CRACKING C-H BONDS
ADDITION REACTIONS
HEPTANE
C_7H_{16}
2-HEPTENE
C_7H_{14}
PROPYLENE
C_3H_6
PROPANE
C_3H_8
1-BUTENE
C_4H_8
BUTADIENE
C_4H_6
METHANE
CH_4
ETHYLENE
C_2H_4
ETHYLENE
C_2H_4
BENZENE
C_6H_6
PROPYNE
C_3H_4
ACETYLENE
C_2H_2
COKE

FEEDSTOCKS AND YIELDS

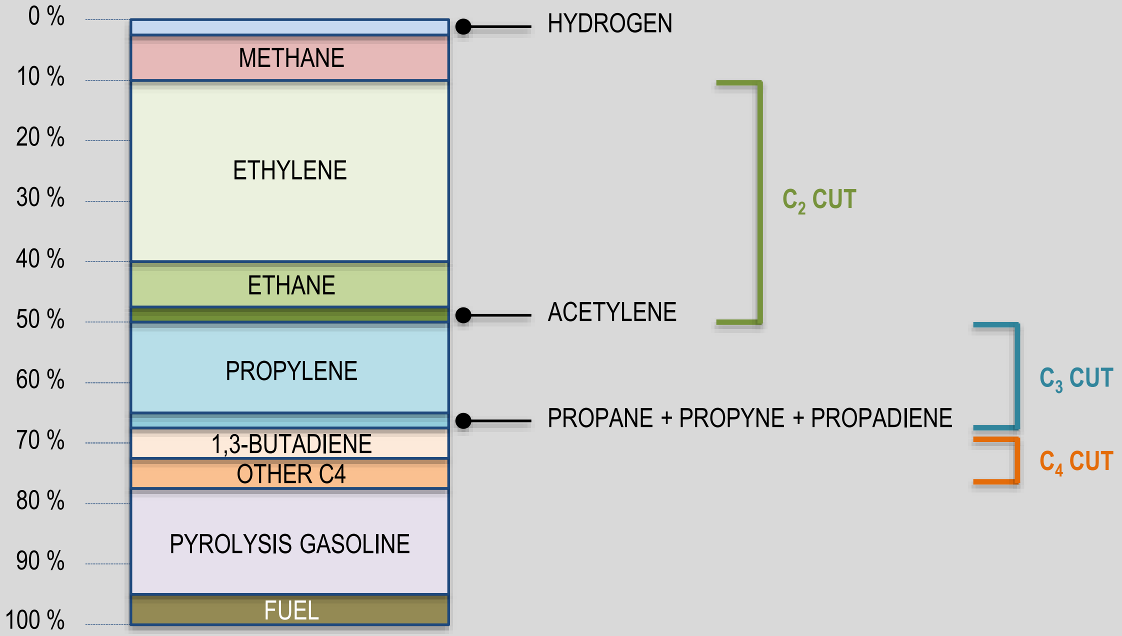
YIELDS FOR NAPHTHA

NAPHTHA

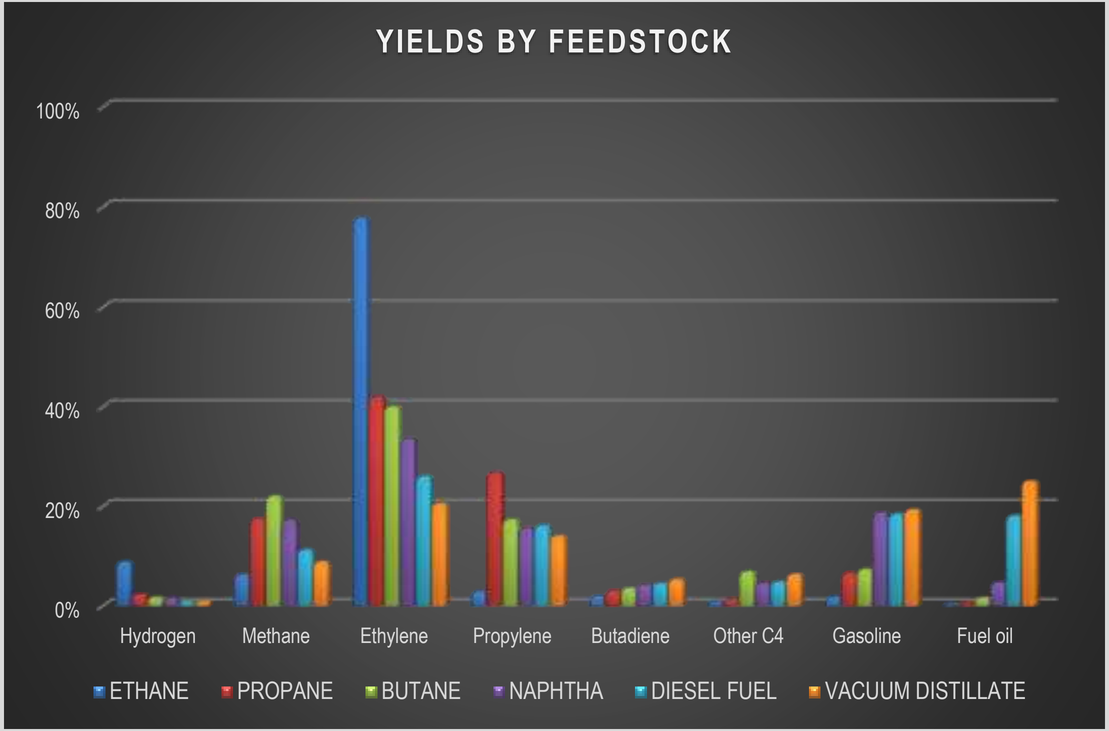
$C_5 - C_6 - C_7$

- ✓ Paraffins
- ✓ Naphthenes
- ✓ Aromatics

STANDARD YIELDS FOR NAPHTHA

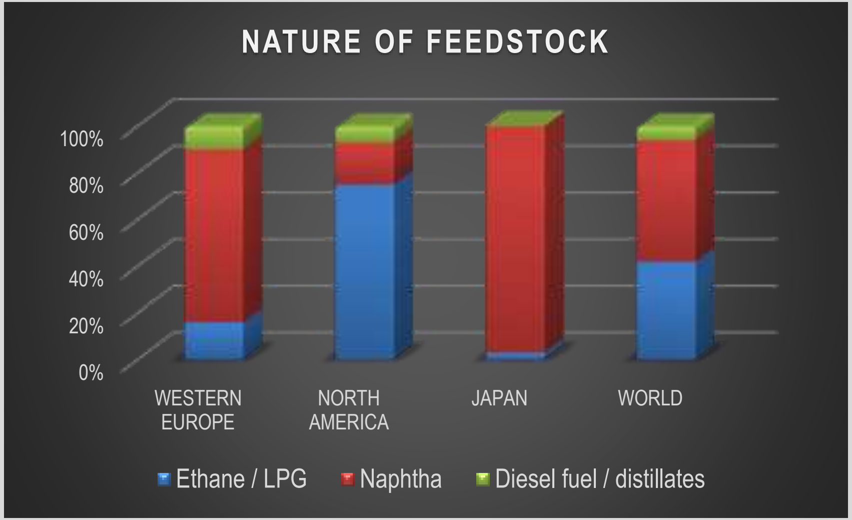


YIELDS FOR VARIOUS FEEDSTOCKS

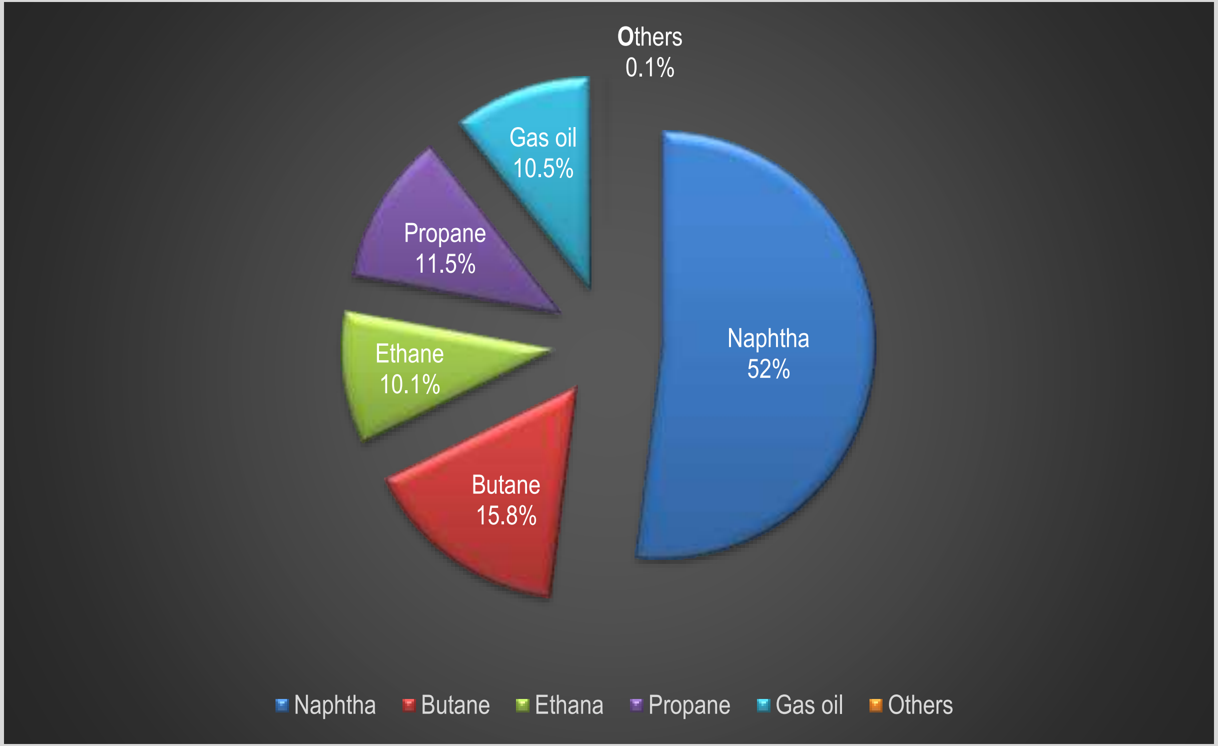


WORLD BREAKDOWN OF FEEDSTOCKS

NATURE OF FEEDSTOCKS	ETHANE LPG	NAPHTHA	DIESEL FUEL DISTILLATES
WESTERN EUROPE	16	74	10
NORTH AMERICA	75	18	7
JAPAN	3	97	-
WORLD	42	52	6



WORLD BREAKDOWN OF FEEDSTOCKS FOR ETHYLENE PRODUCTION



INVESTMENT AND ECONOMICS

INVESTMENT AND ECONOMICS

- ❑ Steam crackers are complex facilities that require **important** investments

- ❑ Key figures for various feedstocks for a **500 kT/year** ethylene production, based in **Europe** :

FEEDSTOCK	ETHANE	NAPHTHA	DIESEL FUEL
Minimum investment (M$)	350 - 400	450 - 550	550 - 650

- ❑ Pyrolysis furnaces account for ~40% of investments (~200M$)

- ❑ The remaining ~60% for separation and purification facilities (~300M$)

INTRODUCTION

INTRODUCTION

- A typical steam cracker plant is made of 3 parts :

1. The hot zone :

- Pyrolysis or cracking furnaces
- Quench exchangers and quench ring
- Separation columns and splitters of the hot separation train

2. The compression zone

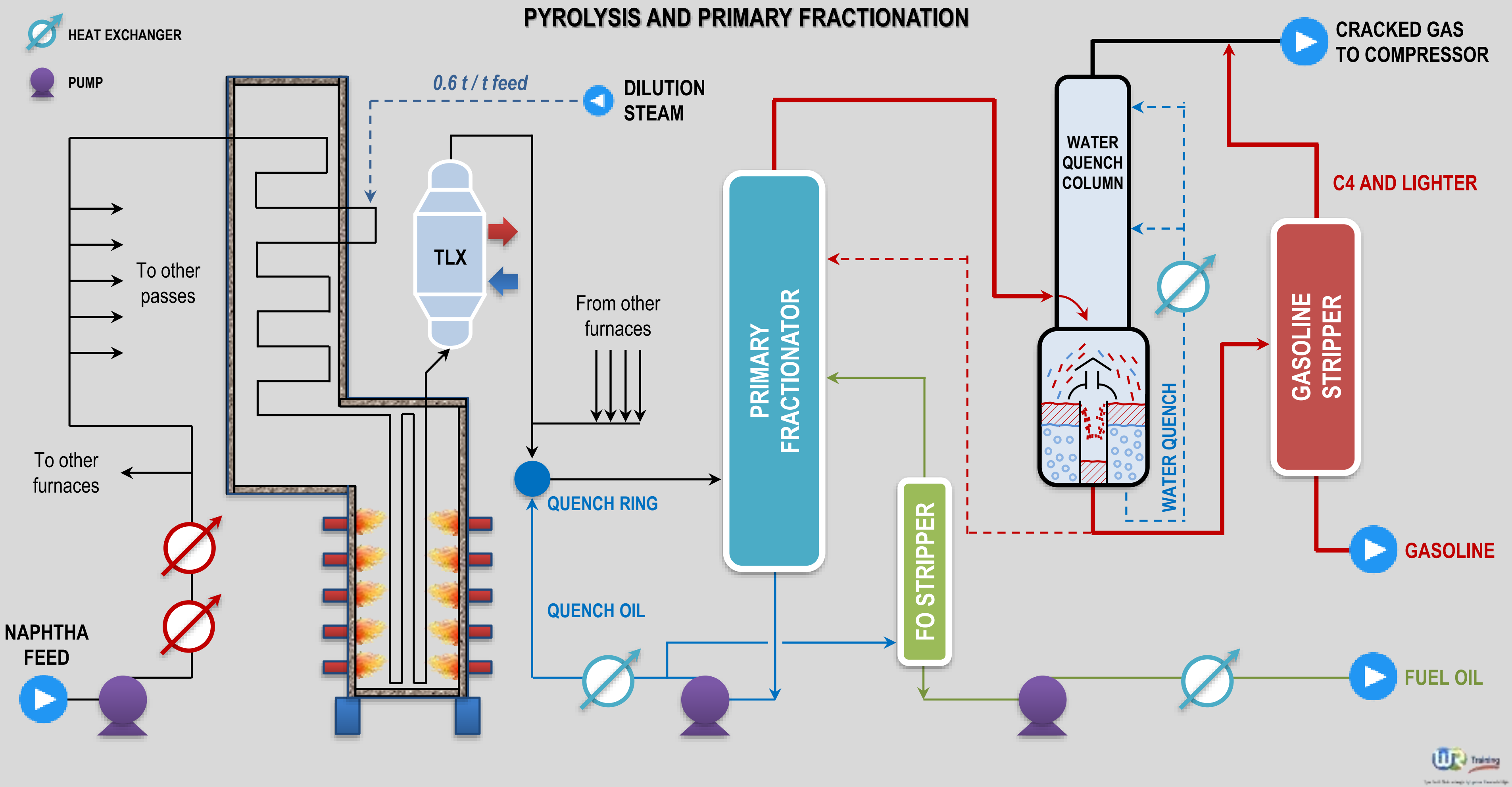
- A cracked gas compressor
- Purification and separation columns
- Dryers

3. The cold zone

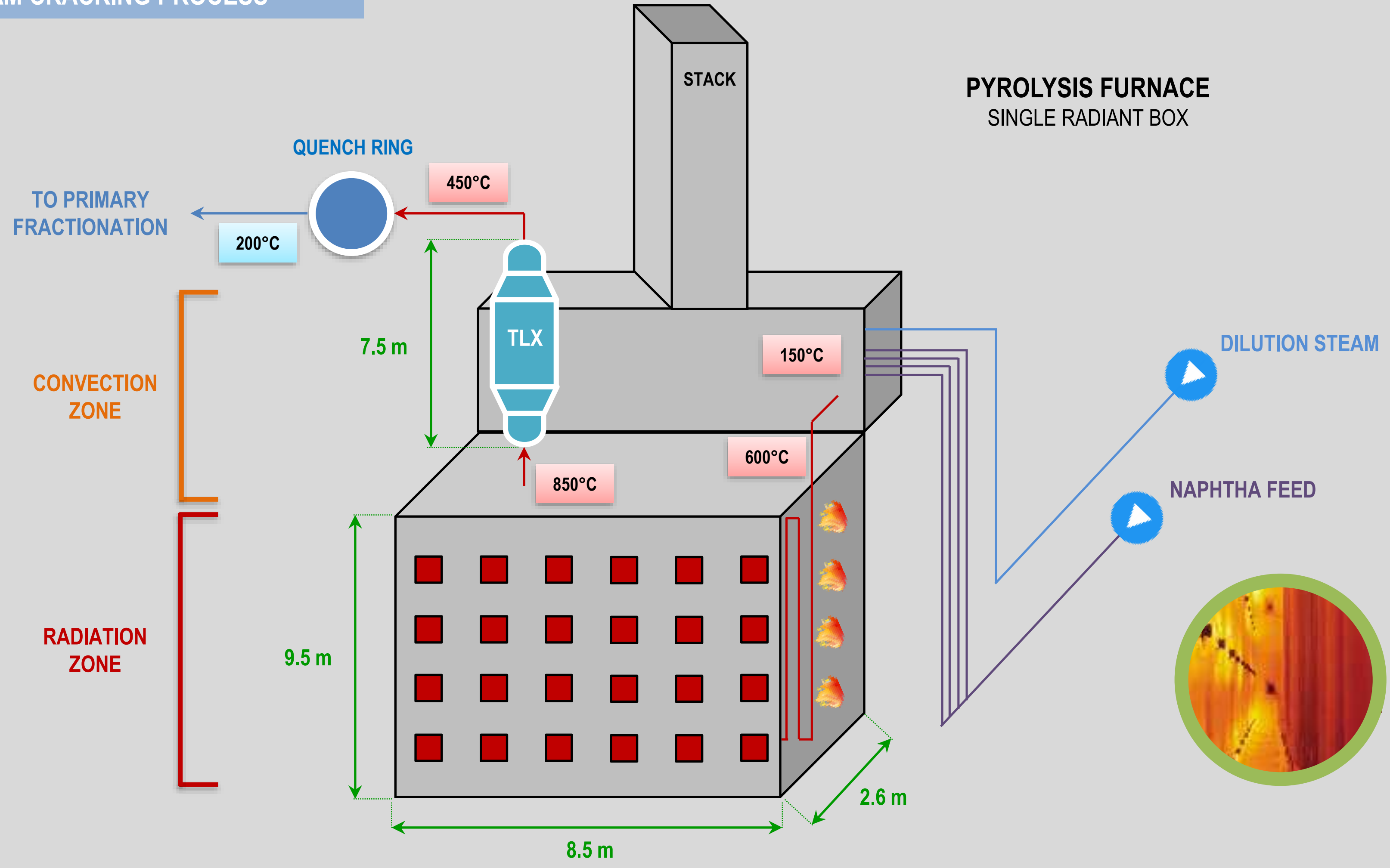
- The cold box
- A methanation reactor
- Separation columns and splitters of the cold separation train
- C2 and C3 converters
- A gasoline hydrostabilization reactor

THE HOT ZONE

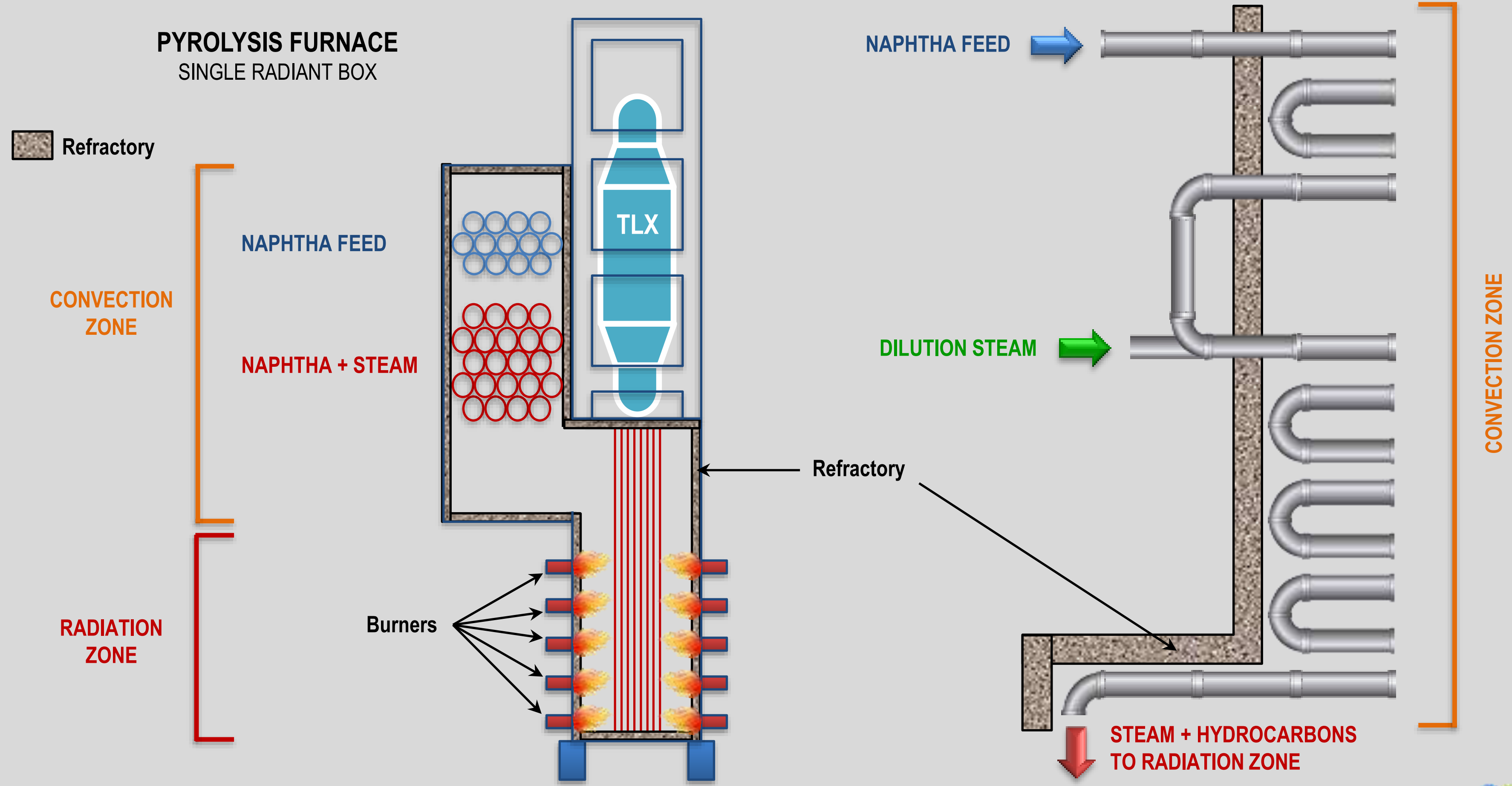
THE STEAM CRACKING PROCESS



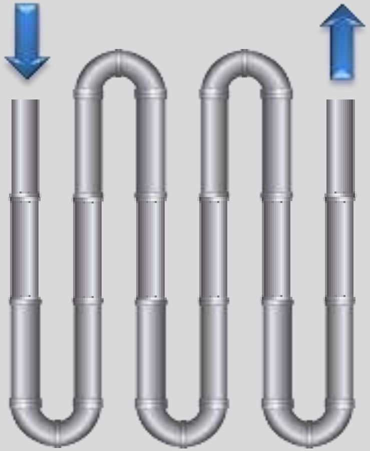
THE STEAM CRACKING PROCESS



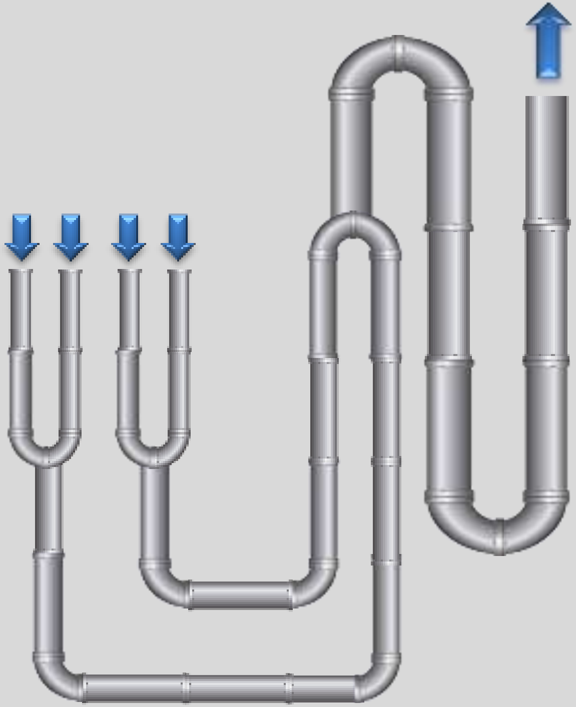
THE STEAM CRACKING PROCESS



THE STEAM CRACKING PROCESS



3-pin coil tubes of same Φ



Coil with tubes of increasing Φ

CONVENTIONAL FURNACES

Single vertical tube

m-SEC FURNACES

PROBLEMS ASSOCIATED WITH STEAM CRACKER FURNACES

- **CREEP :**

Slow elongation due to temperature

- **CARBURIZATION OF THE TUBES :**

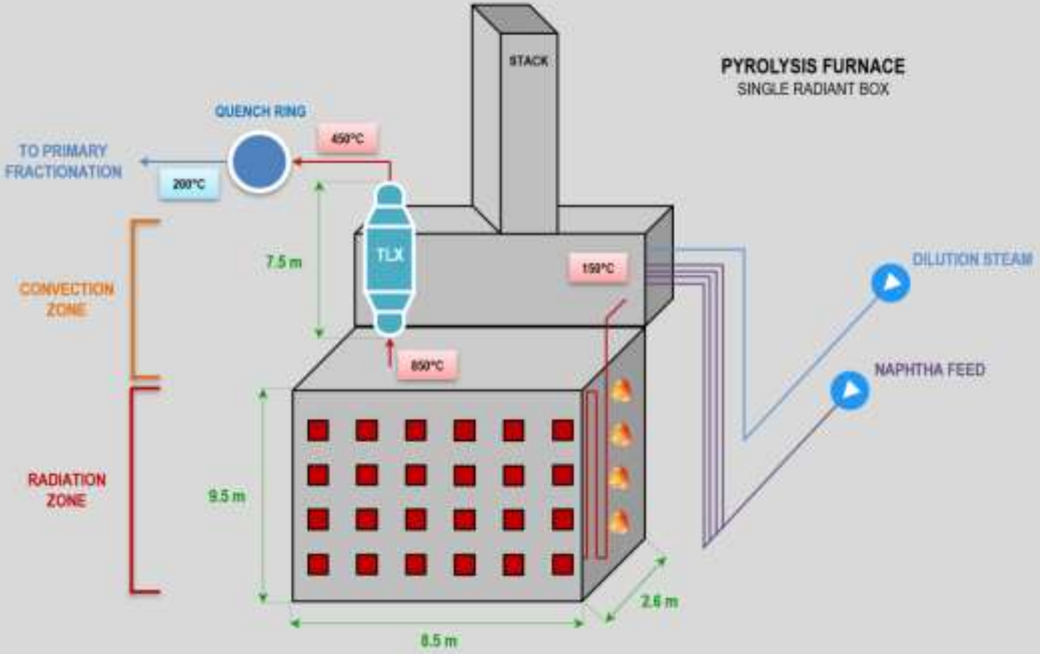
Enrichment in carbon of the tubes from its inside surface

- **EROSION :**

Due to high speed of gases inside the tubes

- **FATIGUE :**

Due to repeated thermal cycles

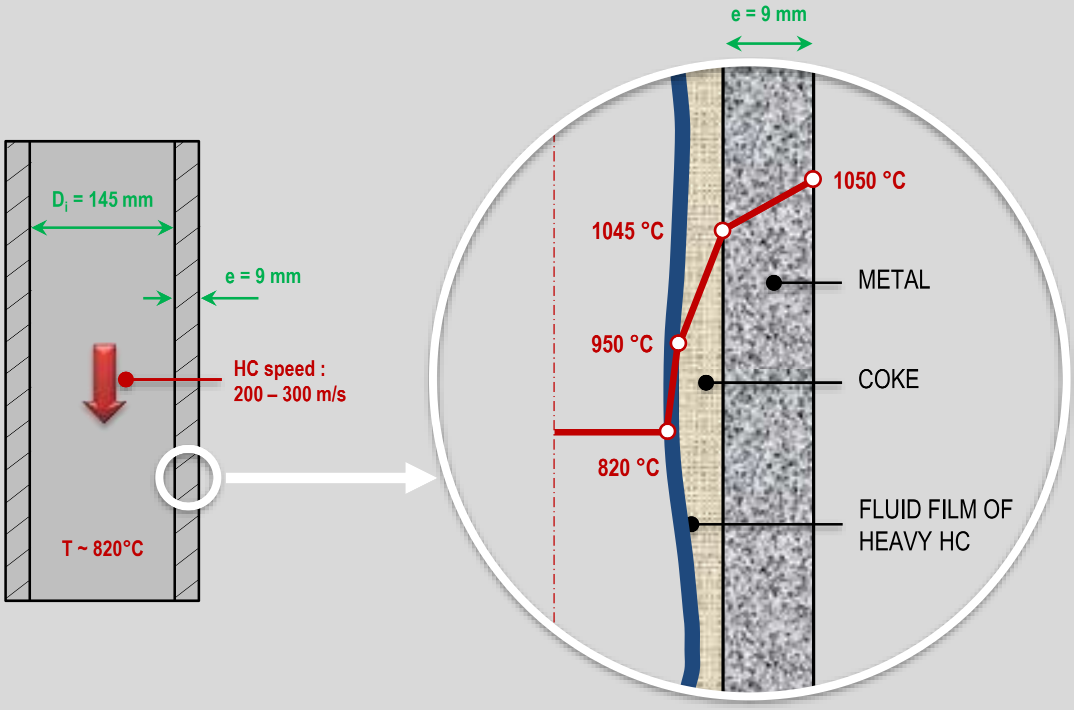


24 Cr CHROMIUM 51.9961 — 30%

28 Ni NICKEL 58.6934 — 35%

6 C CARBON 12.0107 — 0.5%

MECHANISM OF COKE FORMATION

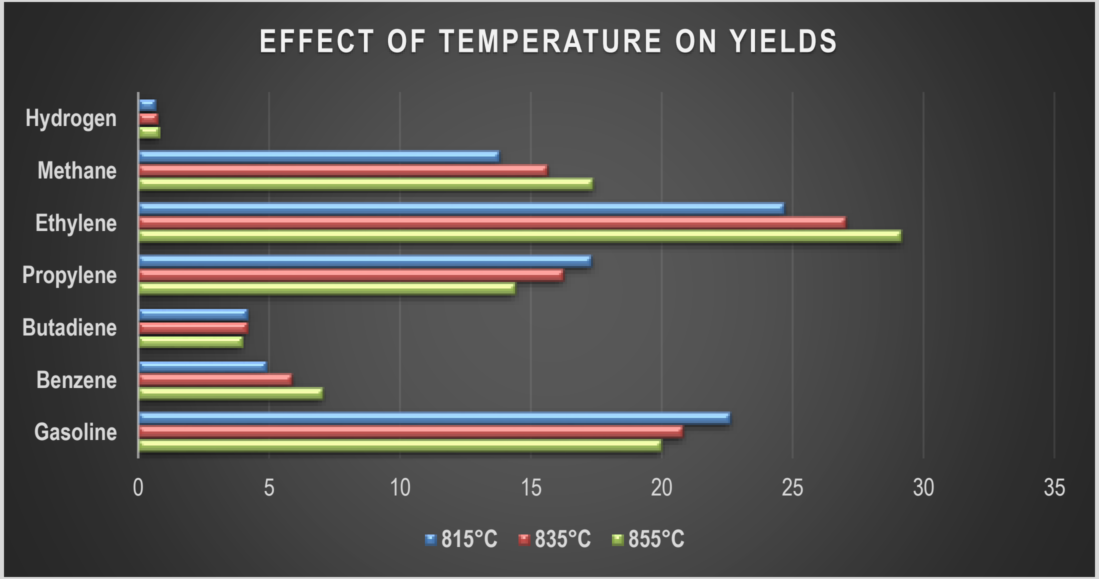


PYROLYSIS FURNACE ADJUSTMENT PARAMETERS

1. Influence of cracking temperature :

NAPHTHA COMPOSITION	% Vol
PARAFFINS	80
NAPHTHENES	15
AROMATICS	5

Dilution steam t/t of feed	0.6

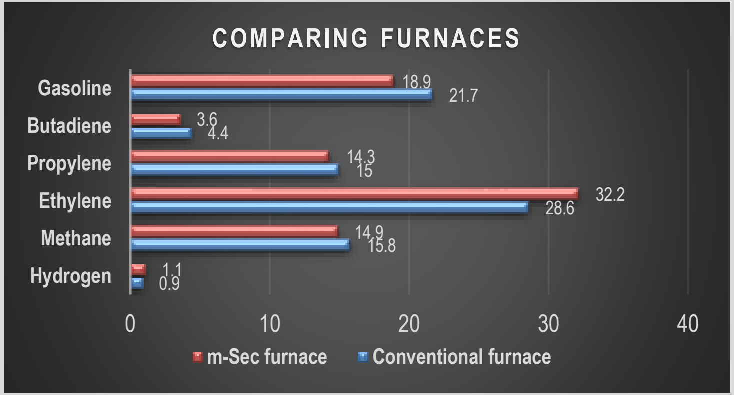


PYROLYSIS FURNACE ADJUSTMENT PARAMETERS

2. Influence of residence time :

- In the 1950's :
  - Residence time ~ 0.7 to 1 sec
  - Ethylene yields ~ 22%
- In the 1960's :
  - Residence time ~ 0.2 to 0.4 sec
  - Ethylene yields ~ 28%
- In the past few years :
  - Residence time ~ 0.05 to 0.1 sec
  - Cracking temperature ~ 900°C

% WEIGHT		CRACKING NAPHTHA Conventional furnace	m-Sec furnace
Hydrogen	H_2	0.9	1.1
Methane	CH_4	15.8	14.9
Ethylene	C_2H_4	**28.6**	**32.2**
Propylene	C_3H_6	15.0	14.3
Butadiene	C_4H_6	4.4	3.6
Gasoline	$C_{5\text{-}200}$	21.7	18.9



PYROLYSIS FURNACE ADJUSTMENT PARAMETERS

3. Influence of pressure :

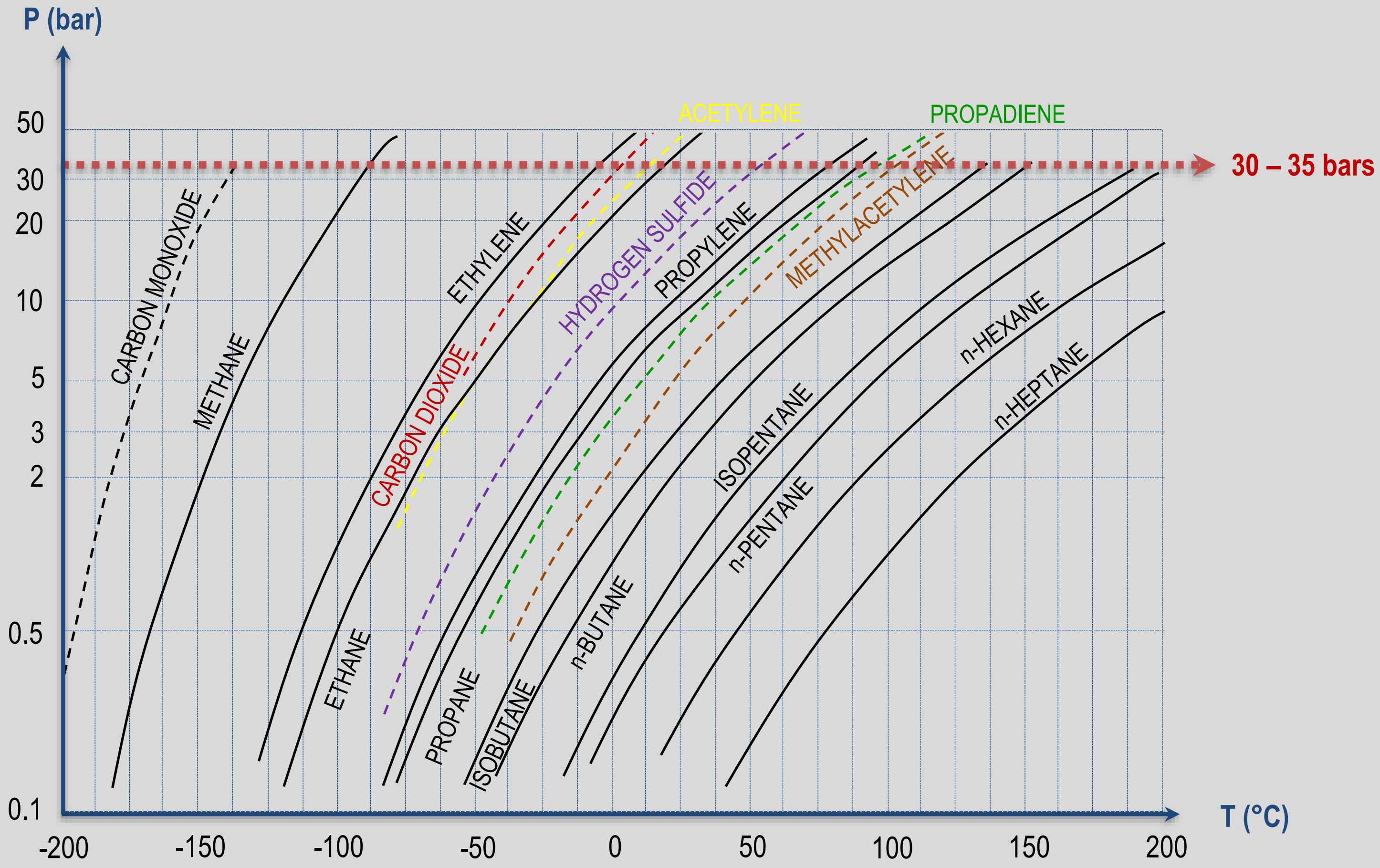
- A lower operating pressure :
  - promotes light olefins formation
  - reduces coke
- Steam cracker furnaces are operated at the lowest pressure possible by :
  - maintaining the output pressure of the furnaces at a value as close as possible to atmospheric pressure
  - reducing the pressure of hydrocarbons by injection of steam

STEAM CRACKER FEED	STEAM (t) / HC (t)
ETHANE – PROPANE – BUTANE	0.3 – 0.4
NAPHTHA	0.5 – 0.6
DIESEL FUEL	0.6 – 0.8

THE COMPRESSION ZONE

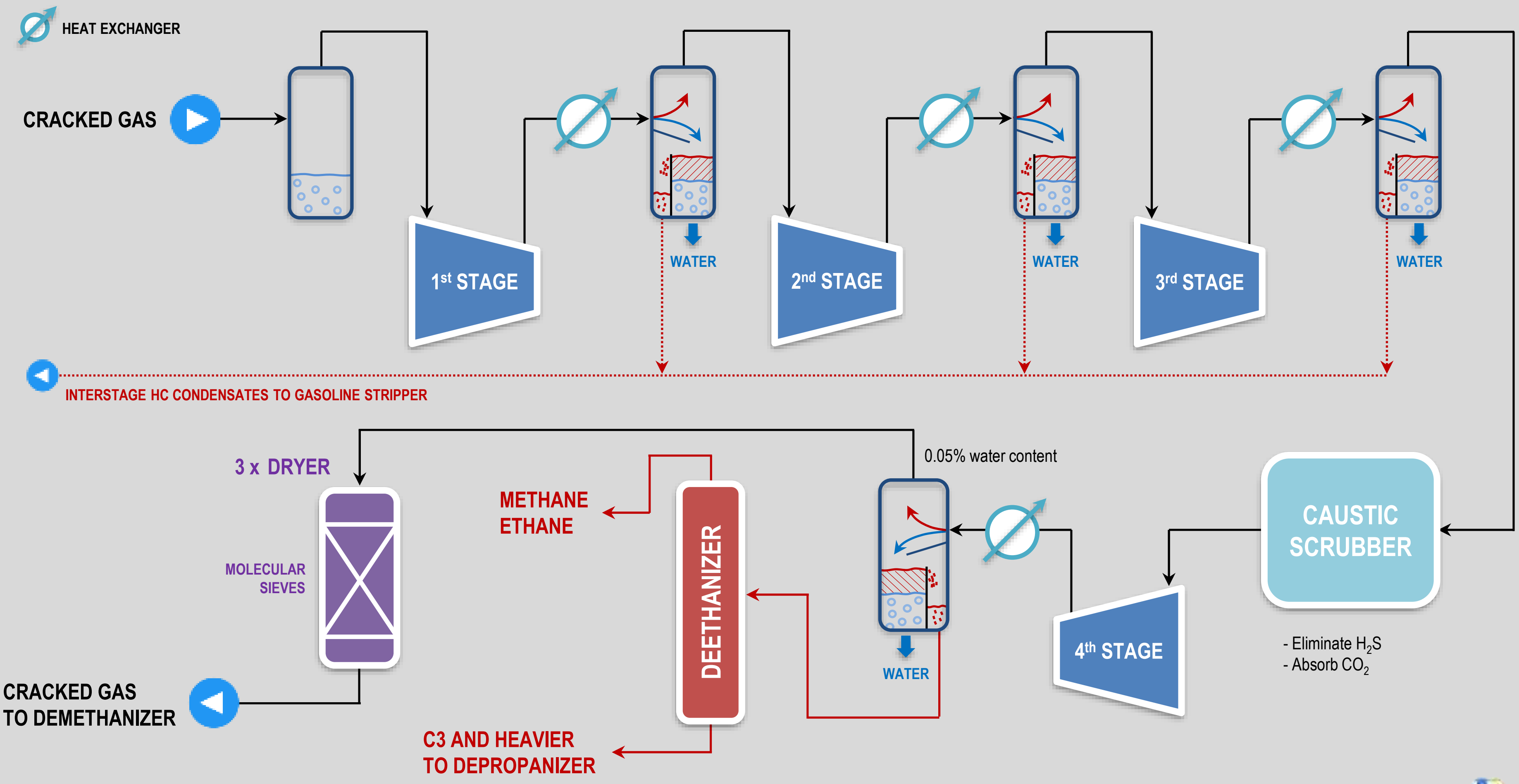
THE STEAM CRACKING PROCESS

PRODUCT	FORMULA	% Weight	
Hydrogen	H_2	1.1	Separation of hydrogen with 95% purity for downstream hydrogenation units
Methane	CH_4	16.2	Recovery of methane for use as internal fuel
Ethylene	C_2H_4	**29.2**	**Required purity : 99.95 % weight**
Acetylene	C_2H_2	0.3	Separated and eliminated
Ethane	C_2H_6	**7.2**	**Recycled back to ethane cracking furnaces**
Carbon monoxide **Carbon dioxide** **Hydrogen sulfide**	CO CO_2 H_2S	**0.15**	**Impurities and catalyst poisons to be removed and eliminated**
Propylene	C_3H_6	**14.3**	**Required purity : 99.5 % weight**
Propane	C_3H_8	0.5	
Propyne Propadiene	C_3H_4 C_3H_4	0.5	Separated and eliminated
C4 cut	-	**8.45**	**Recovery of butadiene and removal of acetylenics**
Gasoline	$C_{5\text{-}200}$	19.8	Elimination of unstable diolefins and **recovery of benzene**
Water	H_2O	**2.3**	Removal of water to avoid clogging at low temperatures by formation of hydrate crystals


P (bar)
50
30
20
10
5
3
2
0.5
0.1
-200
-150
-100
-50
0
50
100
150
200
T (°C)
30 – 35 bars
CARBON MONOXIDE
METHANE
ETHANE
ETHYLENE
CARBON DIOXIDE
ACETYLENE
HYDROGEN SULFIDE
PROPYLENE
PROPANE
ISOBUTANE
n-BUTANE
PROPADIENE
METHYLACETYLENE
ISOPENTANE
n-PENTANE
n-HEXANE
n-HEPTANE

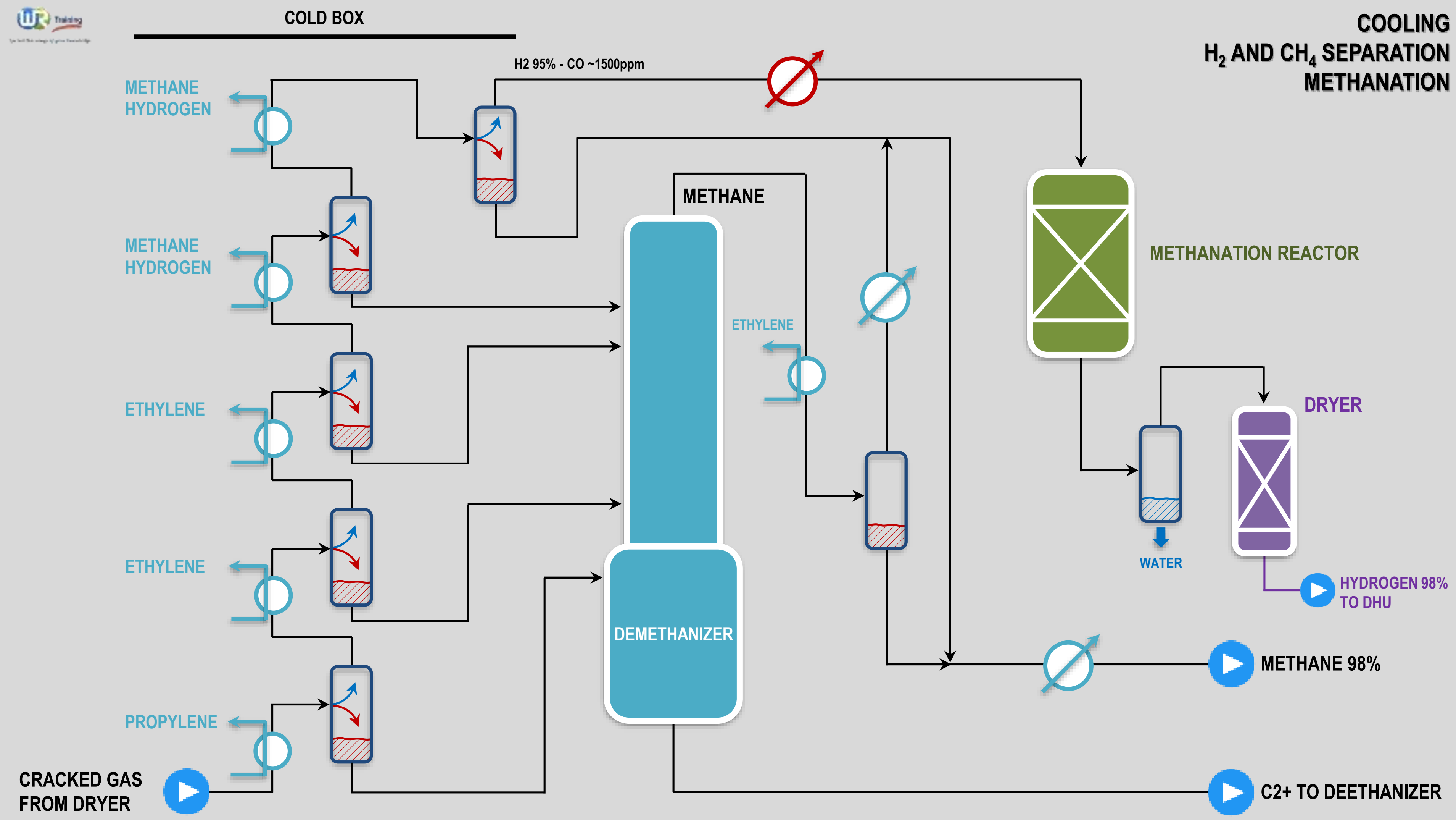
THE STEAM CRACKING PROCESS

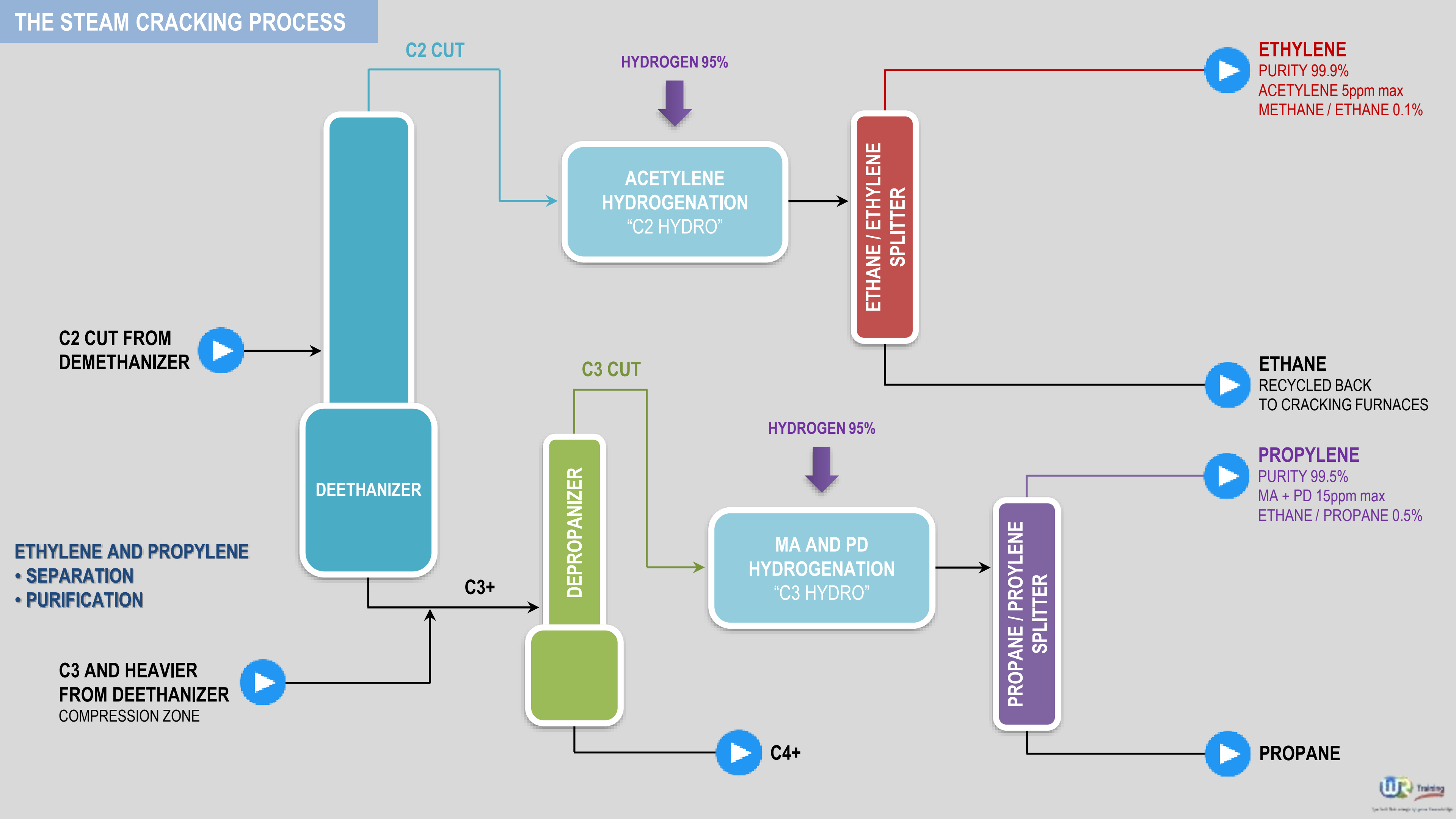
COMPRESSION – WASHING – DRYING



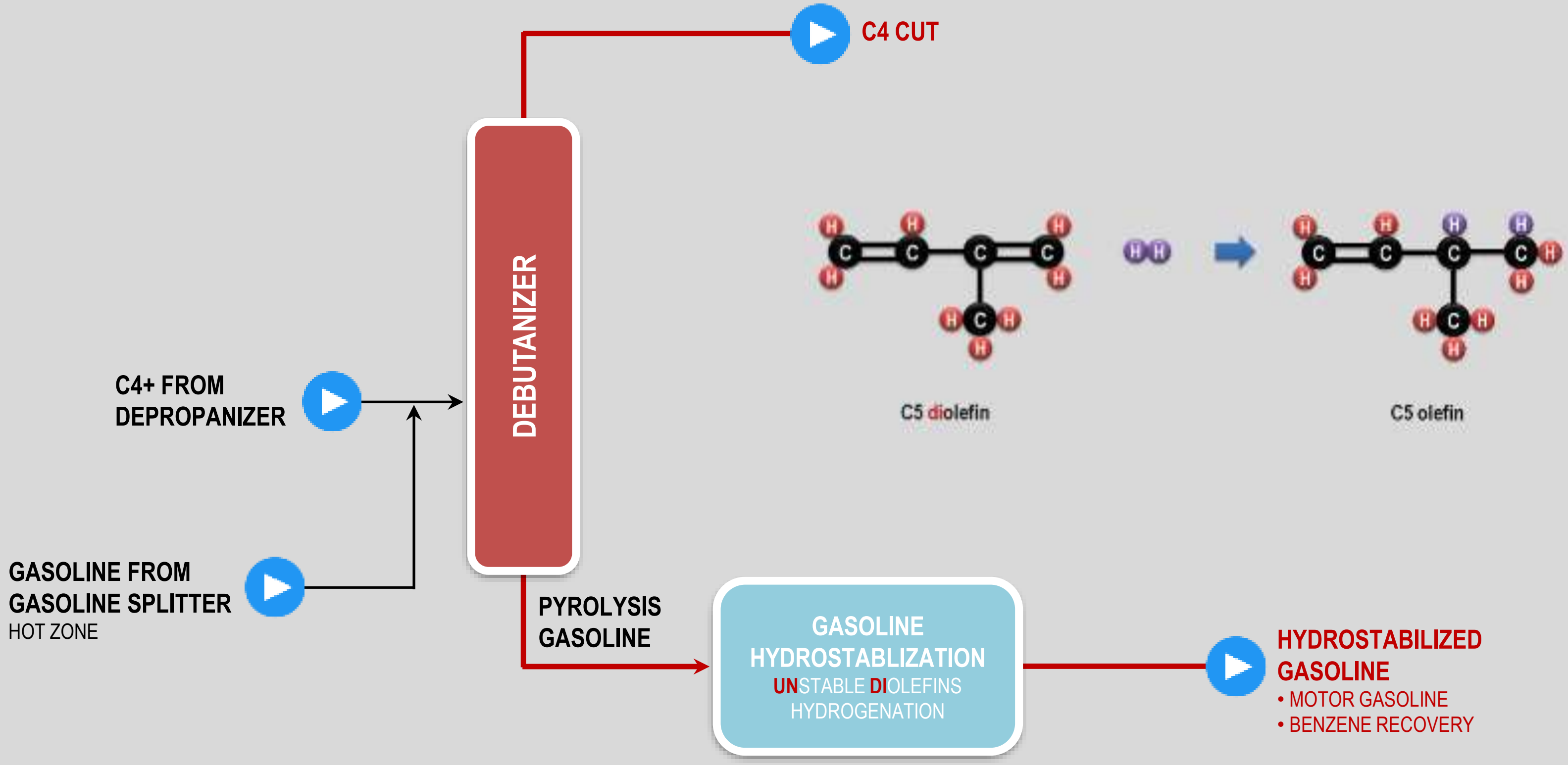
THE COLD ZONE

COOLING
H_2 AND CH_4 SEPARATION
METHANATION




THE STEAM CRACKING PROCESS
C2 CUT
HYDROGEN 95%
ACETYLENE HYDROGENATION "C2 HYDRO"
ETHANE / ETHYLENE SPLITTER
ETHYLENE
PURITY 99.9%
ACETYLENE 5ppm max
METHANE / ETHANE 0.1%
C2 CUT FROM DEMETHANIZER
DEETHANIZER
ETHANE
RECYCLED BACK TO CRACKING FURNACES
C3 CUT
HYDROGEN 95%
PROPYLENE
PURITY 99.5%
MA + PD 15ppm max
ETHANE / PROPANE 0.5%
DEPROPANIZER
MA AND PD HYDROGENATION "C3 HYDRO"
PROPANE / PROYLENE SPLITTER
ETHYLENE AND PROPYLENE
• SEPARATION
• PURIFICATION
C3+
C3 AND HEAVIER FROM DEETHANIZER
COMPRESSION ZONE
C4+
PROPANE

THE STEAM CRACKING PROCESS



C2 CUT : SELECTIVE HYDROGENATION

C2 CUT : SELECTIVE HYDROGENATION

C2 CUT	% Weight
ETHANE	19
ETHYLENE	80
ACETYLENE	1

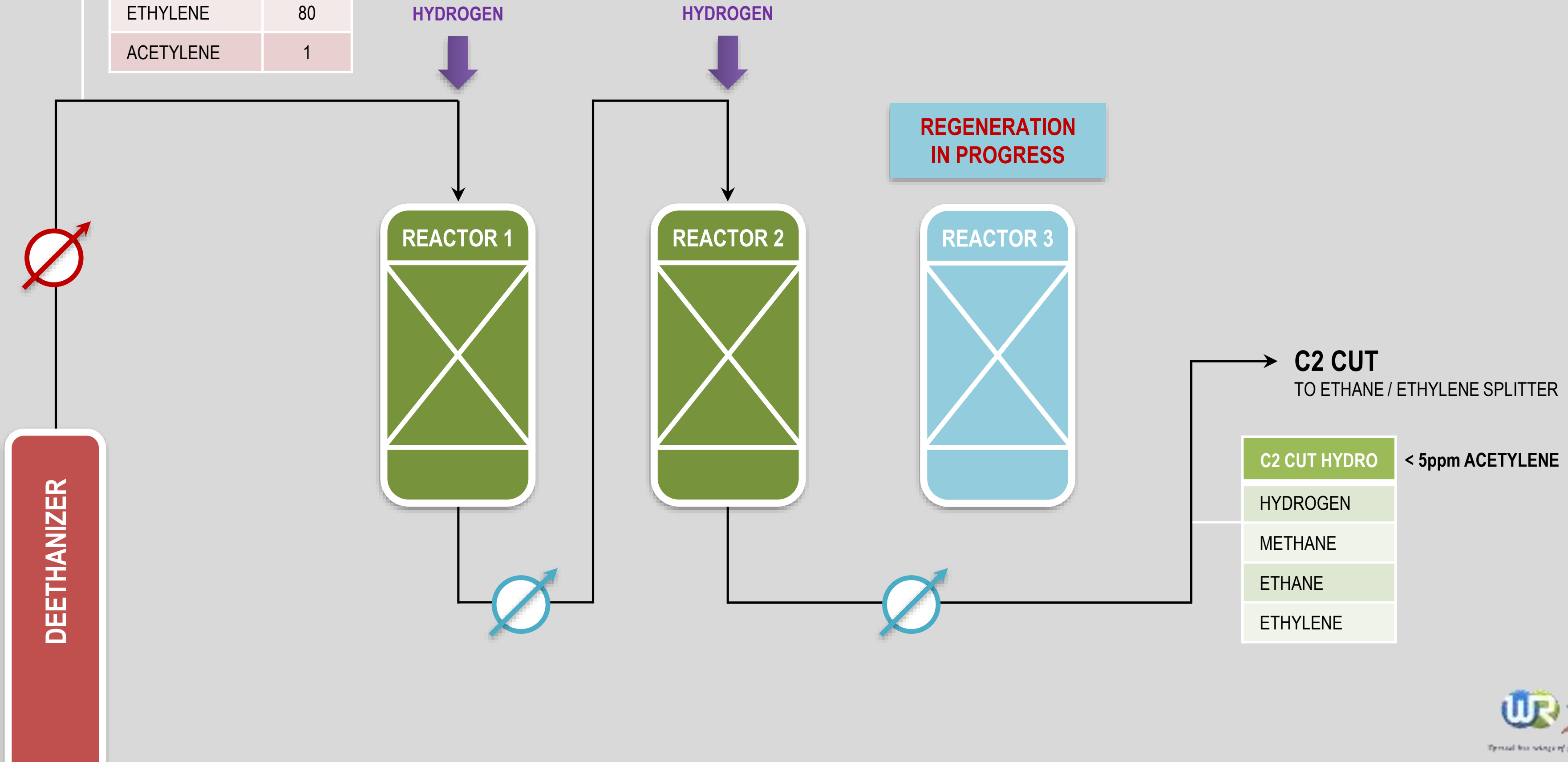
ACETYLENE SPECIFICATION

< 5ppm

< 0.0005%

C2 CUT : SELECTIVE HYDROGENATION

C2 CUT	% VOL
ETHANE	19
ETHYLENE	80
ACETYLENE	1



C2 CUT HYDRO
HYDROGEN
METHANE
ETHANE
ETHYLENE

< 5ppm ACETYLENE

C3 CUT : SELECTIVE HYDROGENATION

C3 CUT : SELECTIVE HYDROGENATION

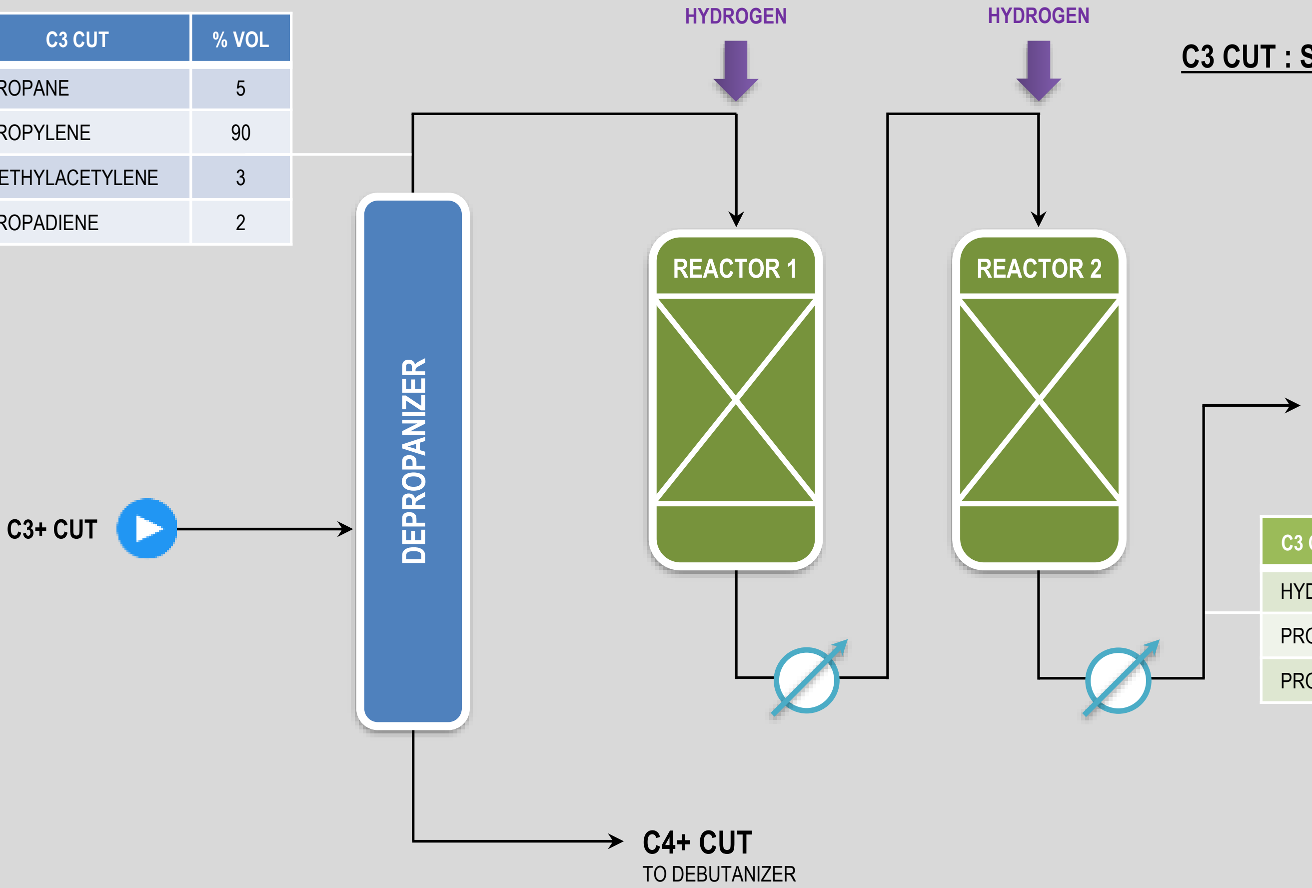
C3 CUT	% Weight
PROPANE	3 – 5
PROPYLENE	85 – 92
PROPYNE	3 – 6
PROPADIENE	2 – 4

PROPYNE / PROPADIENE SPECIFICATION

< 3-4 %

C3 CUT : SELECTIVE HYDROGENATION

C3 CUT	% VOL
PROPANE	5
PROPYLENE	90
METHYLACETYLENE	3
PROPADIENE	2

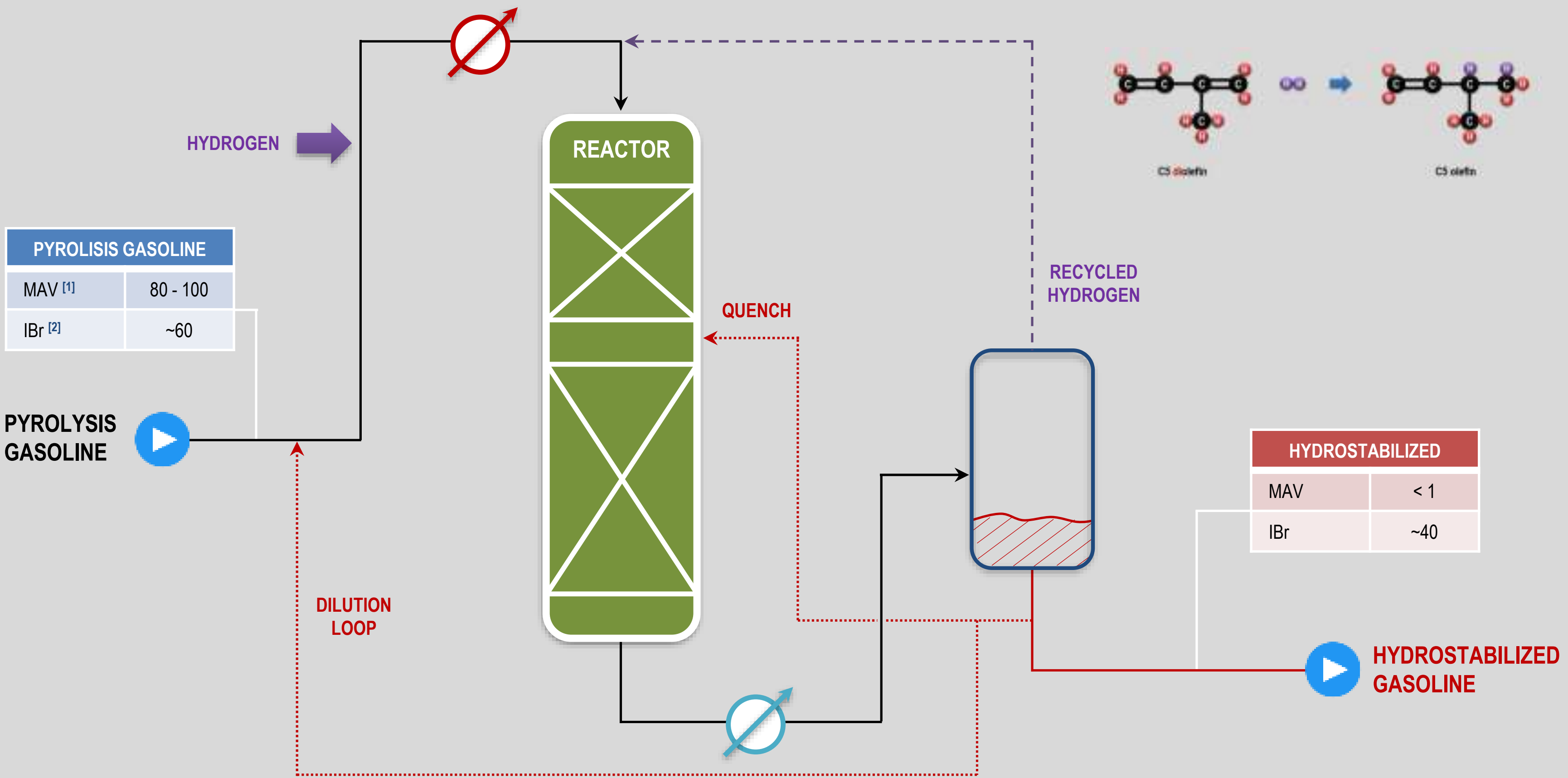


C3 CUT HYDRO
HYDROGEN
PROPANE
PROPYLENE

> 99.5 ppm Polymer grade
> 94% Chemical grade

HYDROSTABILIZATION
OF STEAM CRACKED GASOLINE

SELECTIVE HYDROGENATIONS



PYROLISIS GASOLINE	
MAV [1]	80 - 100
IBr [2]	~60

HYDROSTABILIZED	
MAV	< 1
IBr	~40

[1] Maleic Anhydride Value

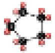
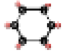
[2] Bromine index

A TYPICAL STEAM CRACKER PLANT

A TYPICAL STEAM CRACKER PLANT

NAPHTHA

$C_5 - C_6 - C_7$

- ✓ Paraffins 
- ✓ Naphthenes 
- ✓ Aromatics 

OTHER FEEDS :

- ETHANE (C2)
- LPG (C3-C4)
- GASOIL (C10-C20)
- DISTILLATES (C20-C40)

STEAM CRACKING

Thermal cracking of hydrocarbons :

✓ at high temperature :

800°C

✓ during a very short time :

0.2 sec

✓ in presence of steam :

0.6 t / t feed

✓ under low pressure :

2-3 bars

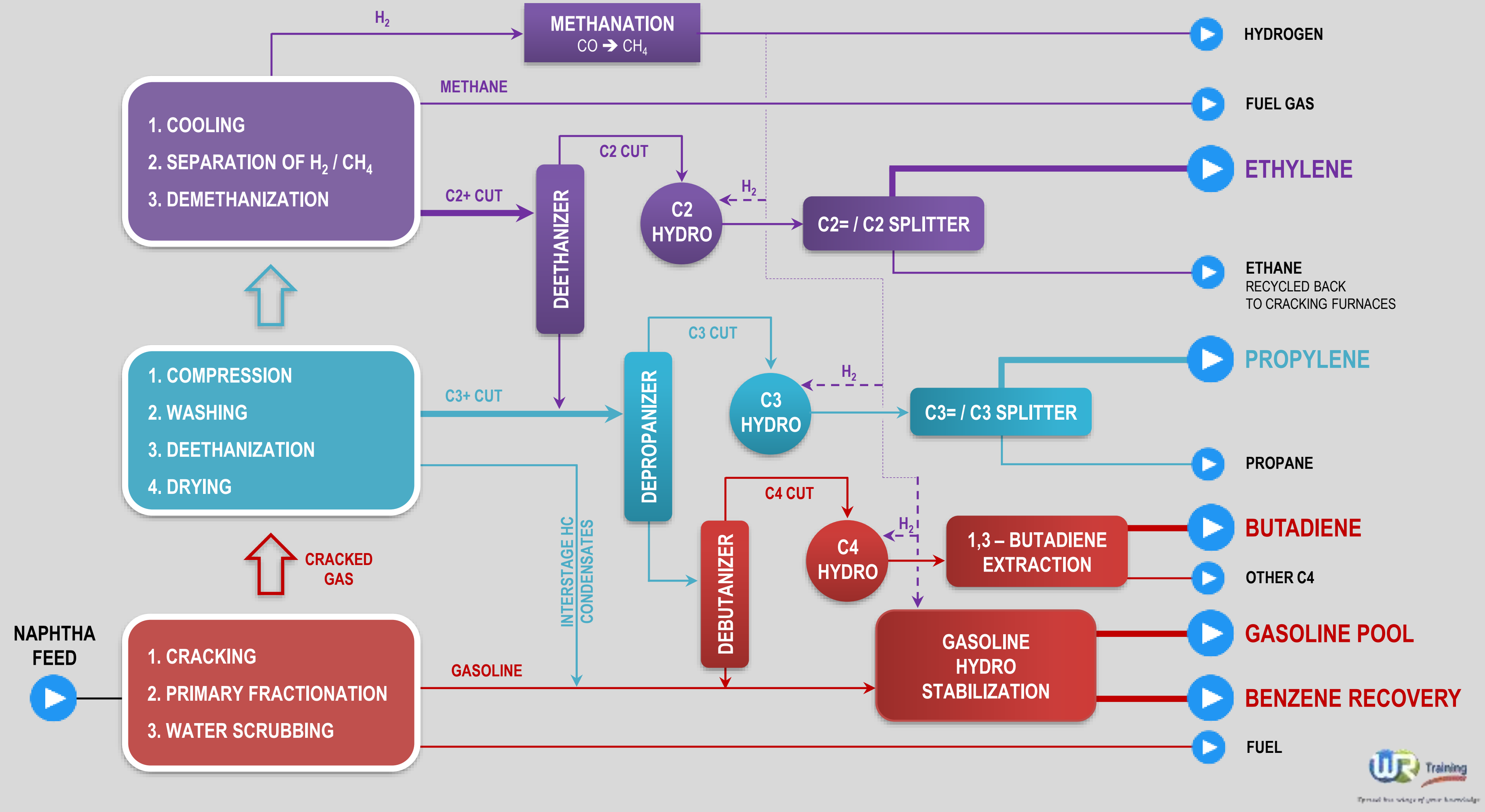
C2 CUT → **ETHYLENE**

C3 CUT → **PROPYLENE**

C4 CUT → **BUTADIENE**

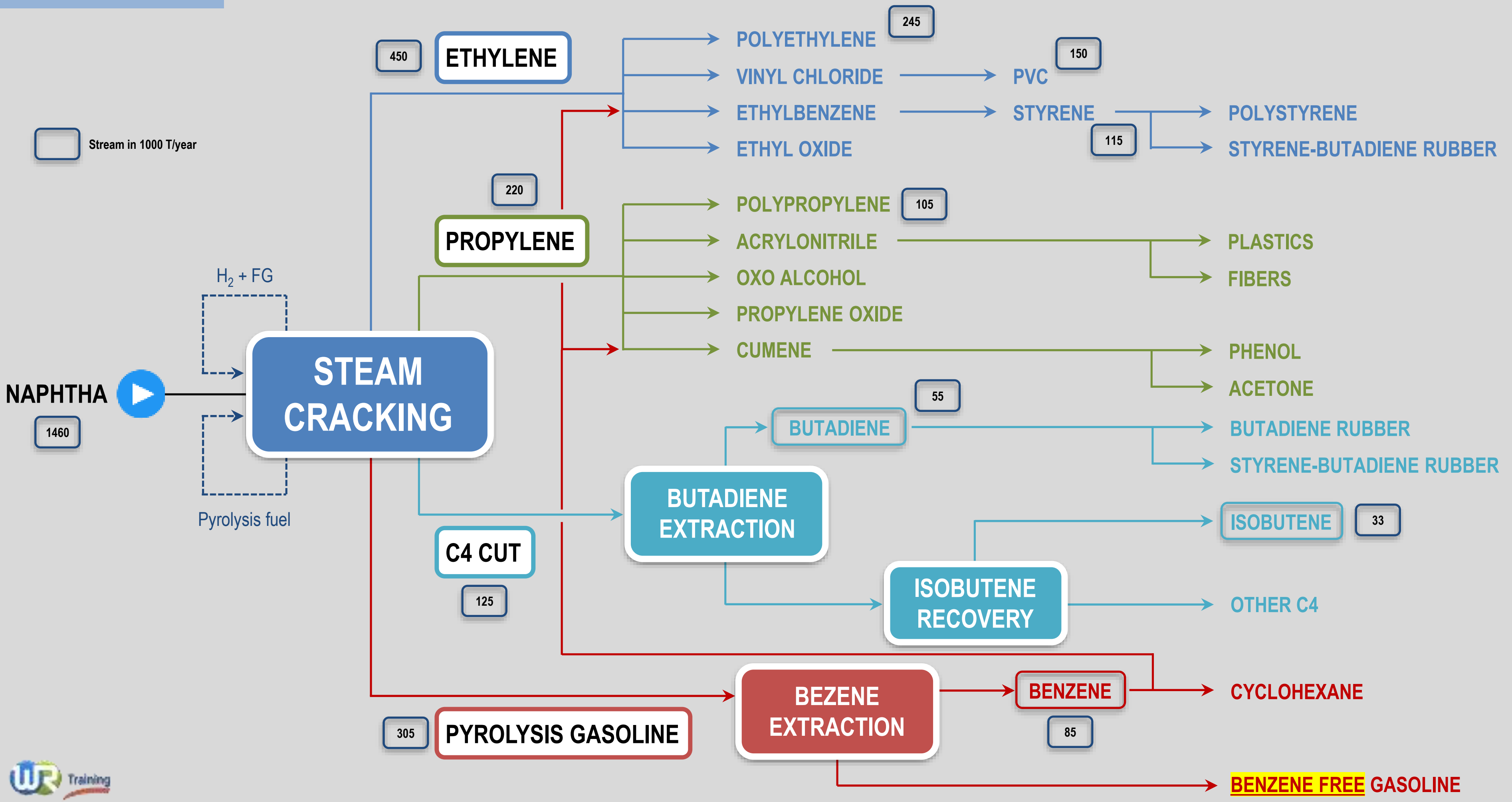
GASOLINE → **BENZENE**

GASOLINE → **AUTOMOTIVE GASOLINE**



METHANATION
CO ➔ CH4
H2
HYDROGEN
METHANE
FUEL GAS
1. COOLING
2. SEPARATION OF H2 / CH4
3. DEMETHANIZATION
C2 CUT
C2+ CUT
DEETHANIZER
C2 HYDRO
H2
C2= / C2 SPLITTER
ETHYLENE
ETHANE
RECYCLED BACK
TO CRACKING FURNACES
C3 CUT
C3+ CUT
DEPROPANIZER
C3 HYDRO
H2
C3= / C3 SPLITTER
PROPYLENE
PROPANE
1. COMPRESSION
2. WASHING
3. DEETHANIZATION
4. DRYING
INTERSTAGE HC CONDENSATES
C4 CUT
DEBUTANIZER
C4 HYDRO
H2
1,3 – BUTADIENE EXTRACTION
BUTADIENE
OTHER C4
CRACKED GAS
NAPHTHA FEED
1. CRACKING
2. PRIMARY FRACTIONATION
3. WATER SCRUBBING
GASOLINE
GASOLINE HYDRO STABILIZATION
GASOLINE POOL
BENZENE RECOVERY
FUEL
Training

WHAT'S NEXT ?


Stream in 1000 T/year
NAPHTHA
1460
H_2 + FG
STEAM CRACKING
Pyrolysis fuel
450
ETHYLENE
220
PROPYLENE
C4 CUT
125
305
PYROLYSIS GASOLINE
POLYETHYLENE
245
VINYL CHLORIDE
PVC
150
ETHYLBENZENE
STYRENE
115
POLYSTYRENE
STYRENE-BUTADIENE RUBBER
ETHYL OXIDE
POLYPROPYLENE
105
ACRYLONITRILE
PLASTICS
FIBERS
OXO ALCOHOL
PROPYLENE OXIDE
CUMENE
PHENOL
ACETONE
BUTADIENE
55
BUTADIENE RUBBER
STYRENE-BUTADIENE RUBBER
BUTADIENE EXTRACTION
ISOBUTENE
33
ISOBUTENE RECOVERY
OTHER C4
BEZENE EXTRACTION
BENZENE
85
CYCLOHEXANE
BENZENE FREE GASOLINE