Coking:

- Coking are severe thermal cracking operations, most commonly used carbon rejection process that upgrades residues to a wide range of lighter H.C gases and distillates through thermal cracking.
- The byproduct of coking process is petroleum coke.
- The goal of coker operation is to maximize the yield of clean distillates and minimize the yield of coke.

Feed stock of coking process:

- Wide variety of feed stocks (can have considerable metals (nickel &vanadium) , sulfur, resin and asphaltens.
- Most contaminants exit with coke.
- Typical feed is vacuum resid.

The main produts:

- Off-gas ⟶ from which LPG is recovered.
- Naphtha ⟶ may be used as gasoline blending agent although its O.N = 65-80 RON.
- Gasoil ⟶ may be catalytic cracking
- Coke ⟶ the main uses of petroleum coke:

1. Fuel
2. Manufacture of anode for electrolytic cell reduction of alumina
3. Direct use as chemical carbon source for manufacture of elemental phosphorus, calcium carbide, and silicon carbide.
4. Manufacture of electrodes for use in electric furnace production of elemental phosphorus, titanium dioxide, calcium carbide, and silicon carbide.
5. Manufacture of graphite.

Types of Coke and their Properties

Coke amount can be up to 30 wt% in delayed coking. It is produced as green coke which requires calcination to remove the volatiles as fuel product. Green coke can also be used as fuel. The most common types of coke are:

Sponge coke

Sponge coke is named for its sponge-like appearance. It is produced from feeds having low to moderate asphaltene content.

Needle coke

This coke has a needle-like structure and is made from feed having no asphaltene contents such as decant oils from FCC. It is used to make expensive graphite electrodes for the steel industry.

Shot coke

This coke is an undesirable product and is produced when feedstock asphaltene content is high and/or when the drum temperature is too high. Discrete mini-balls of 0.1–0.2 in. (2–5 cm) in diameter are rpoduced

Type of coke	Operating condition	Feed characterization	Coke property	End use as calcinated coke
Sponge	Reflux ratio >35% Operating pressure 2–4 bar	Low metal Low *S* Tar residue FCC heavy dist Low to moderate asphaltene	$M < 200$ $S < 2.5\%$ High density >780 HGI[a] ~ 100	Anodes for aluminium industry
Shot	Low pressure Low reflux ratio Large drums	High *S* High metal Low asphaltene	High *S* and metal Low HGI<50 Low surface area	Fuel (green)
Needle	Pressure > 4 bar Reflux ratio = 60–100% to maximize coke yield High temperature to reduce volatile material	High aromatic content Tars, FCC decant Low S <0.5 wt% Low ash <0.1 wt% No asphaltene	Crystalline structure Small needles of high conductivity	Graphite electrodes

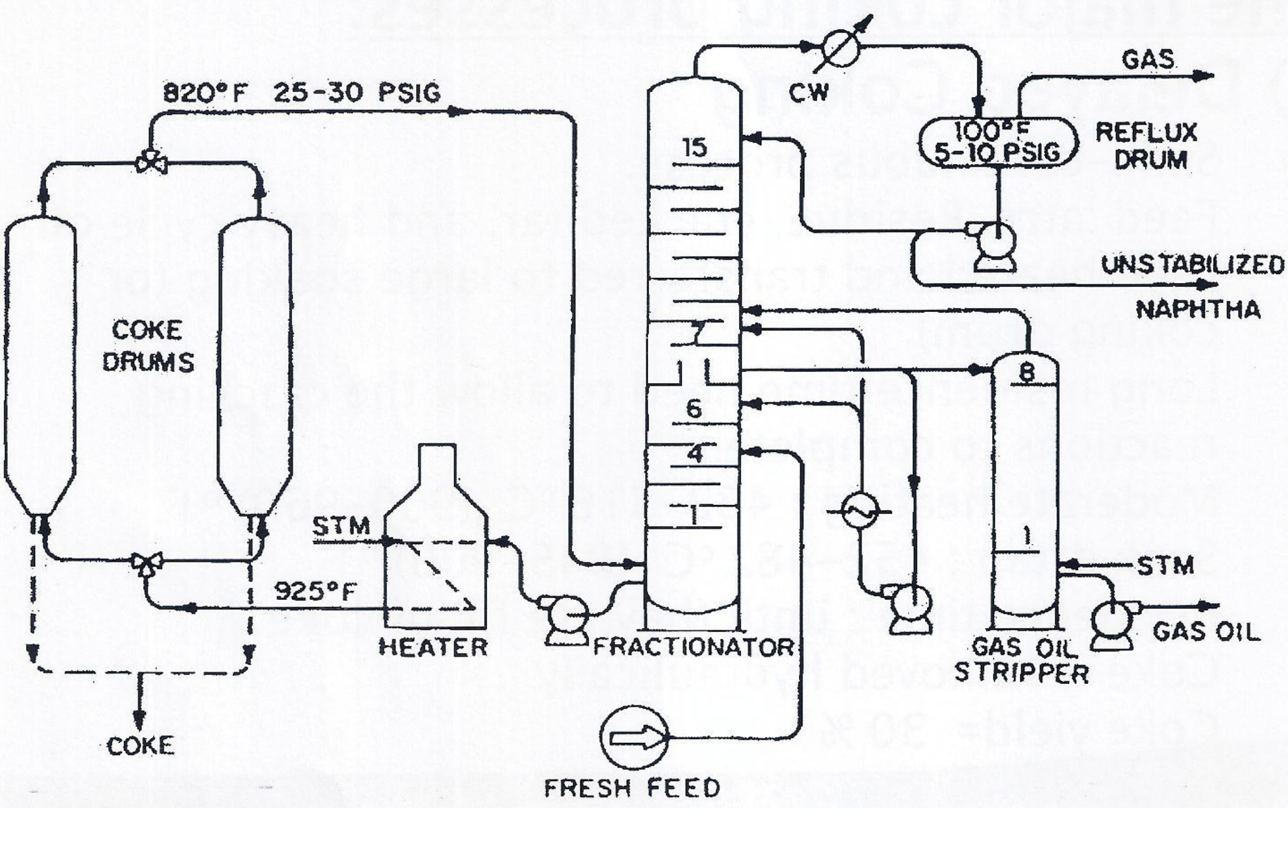
[a]HGI = Hard grove grindability index

The major coking processes:

1) Delayed Coking

- Semi-continuous process.
- Feed :atm. Residue, cracked tar, and heavy cycle oil
- Feed heated and transferred to large soaking (or coking drum).
- Long residence time need to allow the cracking reactions to complete.

1. Moderate heating : 482-516 ºC (900-960) º F
2. Soak drum : 452-482 ºC (845-900) º F
3. Residence time : until they are fill of coke.
4. Coke is removed hydraulically
5. Coke yield= 30 %



Delayed Coker Yield Prediction

Estimation of product yields can be carried out using correlations based on the weight percent of Conradson carbon residue (wt% CCR) in the vacuum residue

$$\text{Gas}(C_4^-)\text{wt\%} = 7.8 + 0.144 \times (\text{wt\% CCR})$$

$$\text{Naphtha wt\%} = 11.29 + 0.343 \times (\text{wt\% CCR})$$

$$\text{Coke wt\%} = 1.6 \times (\text{wt\% CCR})$$

$$\text{Gas oil wt\%} = 100 - \text{Gas wt\%} - \text{Naphtha wt\%} - \text{Coke wt\%}$$

The naphtha can be split in light naphtha (LN) and heavy naphtha (HN). The split in wt% is 33.22 and 66.78, respectively, assuming corresponding gravities of 65 API and 50 API, also respectively.

The gas oil (GO) can be split also into light cycle gas oil (LCO) and heavy cycle gas oil (HCO). The spilt in wt% is 64.5 and 35.5, respectively, and the corresponding gravities are 30 API and 13 API.

Typical sulphur distribution in the products for delayed coking is presented i

Products	Gas	LN	HN	LCO	HCO	Coke
S (wt%)	30	1.7	3.3	15.4	19.6	30

Example

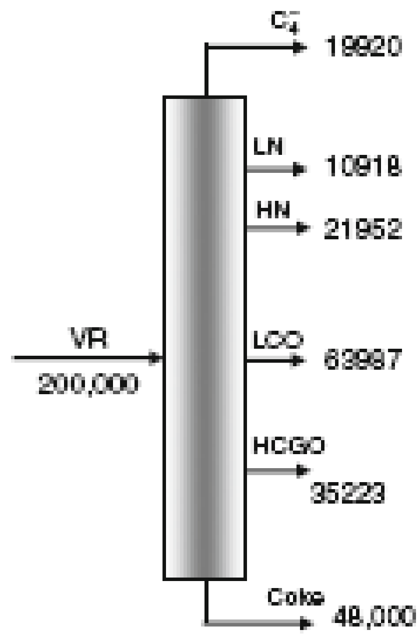
A vacuum residue of Conradson carbon (wt% CCR = 15) is fed into a delayed coker at a rate of 200,000 lb/h, of API= 8.5 and with a sulphur content of 3.0 wt%. Find the amount of yield (lb/h) and their sulphur content. Calculate yield of liquid products in BPD.

Solution:

Table E6.3 Results of delayed coking example

Delayed coker	Feed rate =	200,000	lb/h
	CCR =	15	wt %
	S_f =	3	wt %
	Feed API =	8.5	

Products yield	wt%	lb/h
Gas = (7.8+0.144 × CCR %)	9.96	19,920
Naphtha = (11.29 + 0.343 × CCR%)	16.44	32,870
Coke = (1.6 × CCR%)	24.00	48,000
Gas oil (100 − Gas% − Napthta% − Coke%)	49.61	99,210
	100.00	200,000
Naphtha (assumed split wt%)		
Light naphtha LN = 33.2%	33.22	10,918
Heavy naphtha HN = 66.78%	66.78	21,952
	100.00	32,870
Gas oil (assumed split wt%)		
Light gas oil LGO	64.50	63,987
Heavy gas oil HGO	35.50	35,223
	100.00	99,210
Sulphur distribution in delayed coker products (assumed wt%)		
S in gas	30.00	1800
S in light naphtha	1.70	102
S in heavy naphtha	3.30	198
S in light gas oil	15.40	924
S in heavy gas oil	19.60	1176
S in coke	30.00	1800
	100.00	6000

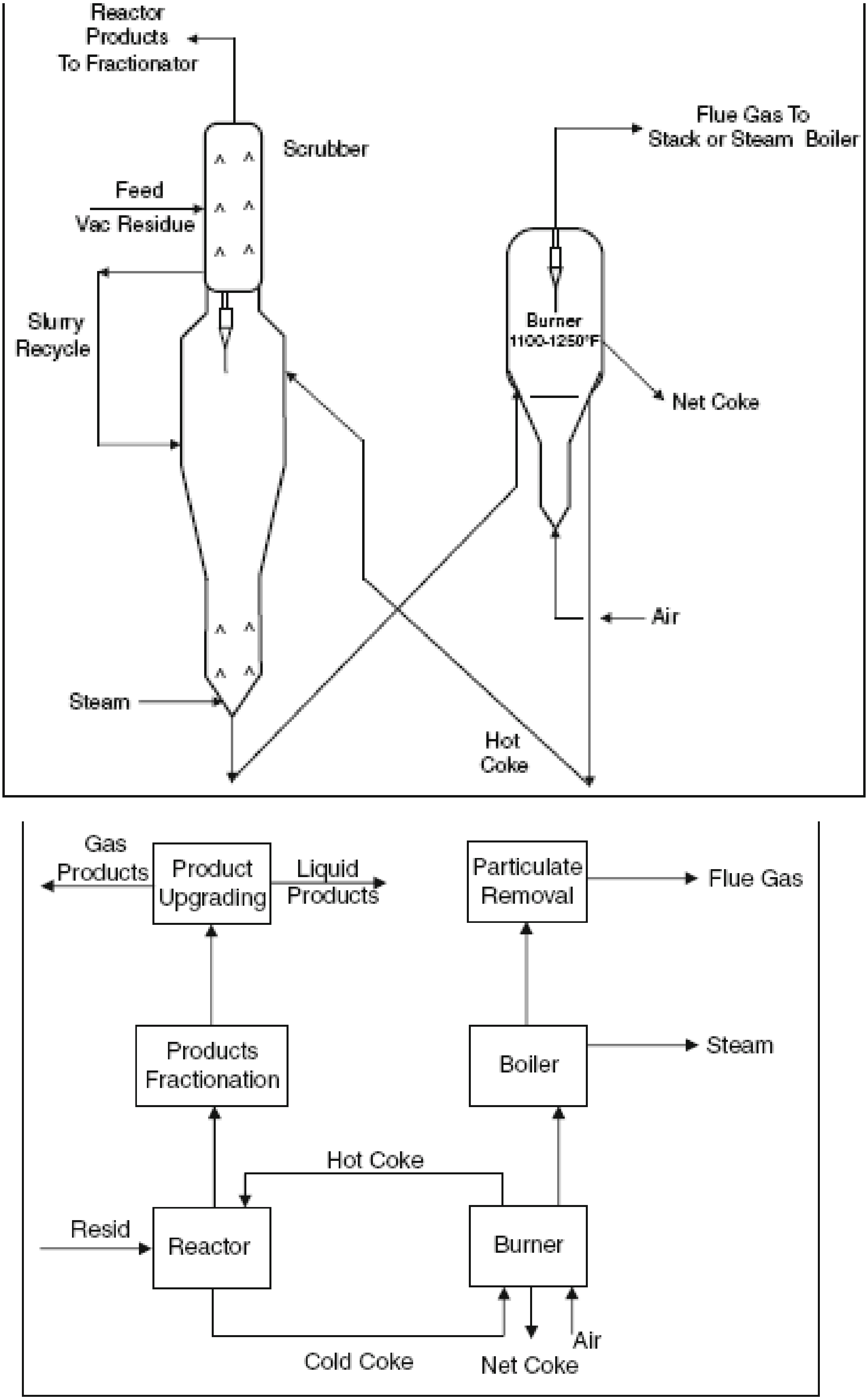


Delayed coker	Feed rate =	200,000	lb/h
	CCR =	15	wt%
	S_f =	3	wt%
	Feed API =	8.5	

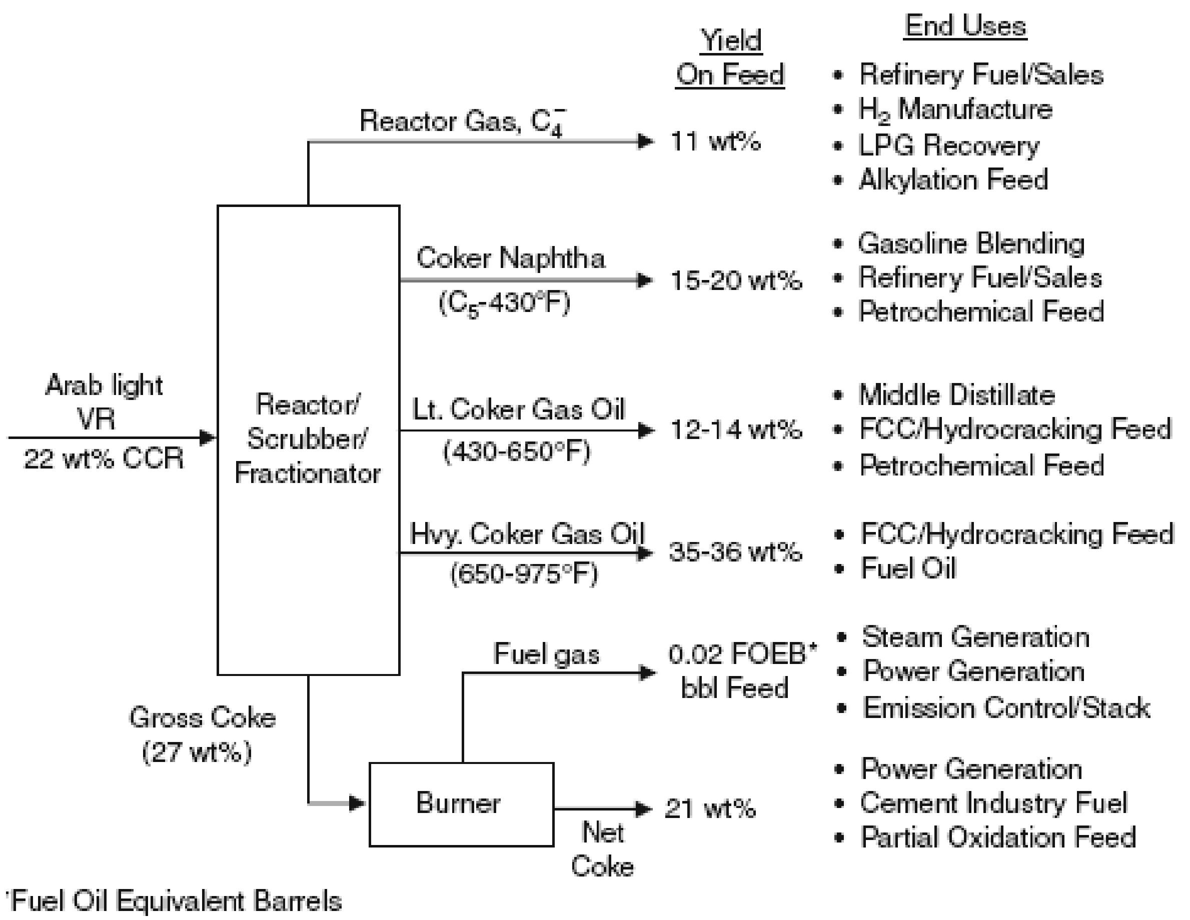
Gravity of products (assumed gravities)	API	SG	BPD
Light naphtha	65	0.72	1041.5
Heavy naphtha	50	0.78	2894.3
Light gas oil	30	0.88	4994.0
Heavy gas oil	13	0.98	2468.5

2) Fluid Coking or flexicoking

- A continuous process which uses the fluidized- solids technique to convert residues to more valuable products.
- The residue is coked by being sprayed into a fluidized bed of hot, fine coke particles.
- The use of a fluid bed permits the coking reaction to be conducted at higher temperature and shorter contact times than those in delayed coking: Fluidized bed with steam.
- Severe heating 482- 566 °C (900-1050) ° F at 10 psig.
- Higher yields of light ends.
- Less coke yields (20 % for fluid coking and 2 % for flexicoking



6.8 Block diagram of fluid coking



A vacuum residue with Conradson carbon of (wt% CCR = 15) is fed into a fluid coker at a rate of 200,000 lb/h, API = 8.5 and with a sulphur content of 3.0 wt%. Find the amounts of products and their sulphur content using the yield guidelines given in Figure 6.9.

Solution:

The solution of the example is summarized in Table E6.5.

Table E6.5 Summary of fluid coking summary results

Feed rate		200,000 lb/h
CCR	15 wt%	
S_f	3 wt%	
Products	**wt%**	**lb/h**
Gases	11	22,000
Naphtha	18	36,000
Light gas oil	14	28,000
Heavy gas oil	36	72,000
Coke	21	42,000
Total	100	200,000

6.7.1. Yield Correlations for Flexicoking

The yield correlations for flexicoking are based on the Conradson carbon content of the vacuum residue (CCR, wt%), its API gravity and sulphur content (S_f). Data compiled by Maples (1993) are correlated to express weight percent yields.

$$\text{Gas wt\%} = 0.171943 \times \text{CCR wt\%} + 5.206667 \tag{6.27}$$

$$\text{Gasoline wt\%} = -0.115234 \times \text{CCR wt\%} + 18.594587 \tag{6.28}$$

$$\text{Coke wt\%} = 1.037233 \times \text{CCR wt\%} + 1.875742 \tag{6.29}$$

$$\text{Gas oil wt\%} = 100 - \text{Gas wt\%} - \text{Gasoline wt\%} - \text{Coke wt\%} \tag{6.30}$$

Gas composition:

$$C_4 \text{ wt\%} = -0.028627 \times \text{CCR wt\%} + 3.200754 \tag{6.31}$$

$$C_2^- \text{ wt\%} = 0.647791 \times [\text{Gas wt\%} - C_4 \text{ wt\%}] + 0.456001 \tag{6.32}$$

$$C_3 \text{ wt\%} = \text{Gas wt\%} - C_4 \text{ wt\%} - C_2^- \text{ wt\%} \tag{6.33}$$

Sulphur distribution in products:

$$S \text{ wt\% in Gasoline} = 0.193461 S_f \tag{6.34}$$

$$S \text{ wt\% in Gas oil} = 0.91482 S_f + 0.16921 \tag{6.35}$$

$$S \text{ wt\% in Coke} = 1.399667 S_f + 0.18691 \tag{6.36}$$

$$S \text{ in Gas} = S \text{ in Feed} - S \text{ in Gasoline} - S \text{ in Gas oil} - S \text{ in Coke} \tag{6.37}$$

Gravity of flexicoker feed and gas oil

$$\text{Feed API}_f = 0.5 \times \text{CCR wt\%} + 0.932644 \tag{6.38}$$

$$\text{Gas oil API} = 1.264942 \times \text{API}_f + 0.506675 \times \text{CCR wt\%} - 0.79976 \tag{6.39}$$

Example E6.6

Resolve example E6.1 for the case of flexicoking.

Solution:

The result of this example for flexicoking is given in Table E6.6.

Table E6.6 Flexicoking example

	Feed rate =	200,000	lb/h
	CCR =	15	wt%
Flexicoking	S_f =	3	wt%
	Feed API =	8.5	
Products yield		**wt%**	**lb/h**
Gas wt% = (0.171943 × CCR% + 5.206667)		7.79	15,572
Gasoline wt% = (−0.115234 × CCR% + 18.594587)		16.87	33,732
Coke wt% = (1.037233 × CCR% + 1.875742)		17.43	34,868
Gas oil wt% = (100 − Gas% − Gasoline% − Coke%)		57.91	115,828
		100.00	200,000
Gases			
C_4 wt% = (−0.028627 × CCR% + 3.200754)		2.77	5543
C_2^- wt% = (0.647791 × (Gas% − C_4%) + 0.456001)		3.70	7409
C_3 wt% = (Gas% − C_4% − C_2^- %)		1.31	2620
		7.79	15,572
Sulphur in flexicoker products			
S in Gasoline = (0.193461 S_f)		0.58	196
S in Gas oil = (0.91482 S_f + 0.16921)		2.91	3375
S in Coke = (1.399667 S_f + 0.18691)		4.39	1529
S Gas = (*S* Feed − *S* in Gasoline − *S* in Gas oil − *S* in Coke)		0.06	900
			6000
Gravity of flexicoker products		**API**	**SG**
Gas oil API = (1.264942 × API_f + 0.506675 × CCR% − 0.79976)		17.6	0.95
Feed API = (0.5 × CCR% + 0.932644)		8.43	1.00