

Solar-Thermo Chemical Reactions

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Abstract: The regularities of pyrolysis and gasification processes of fuel-oil at solar furnace at the temperature range 500-1000°C have been studied. In most favorable condition 65% of fuel-oil at pyrolysis and 84% at gasification in turn to gaseous products. The content of olefin in gaseous products reaches to 55% mass. The specific energy consumption for gas production is $\varepsilon=1.9\text{kwh/m}^3$, energy effectively is $\eta=67\%$ the accumulation degree of solar energy in fuel gas formation reach to 30%. Some kinetics and thermodynamics issues of solar thermal transformations of fuel-oil have been discussed. The results of investigations of gas formation regularities at conversions of fuel-oil have been discussed.

Key words: Solar-thermal, Gasification, Thermodynamics, Solar energy, Accumulation, Pyrolysis.

Introduction

The refining of heavy petroleum fractions demands large power expenditures. If the depth of light fractions demands for refining the power expenditures 1800-2800 MJ/t, but for fuel-oil and tar this quantity equals 4800 MJ/t. At the high degree refining of petroleum up to 18% of petroleum are burnt down for heat support of technological processes. The increase portion of petroleum use as a fuel also result in unfavorable ecological consequences. That is why, last time it is conducted widely the search on development the non-traditions technology of heavy petroleum refining with the use of solar energy. Iran (Yazd, Khozistan, Sistan and Baluchestan, Hormozgan) is rich in resources of solar energy ($\varepsilon=0.95\text{ kw/m}^2$) and petroleum. In this connection for Iran the design of such processes has a great signification. There are limited works on solar-thermal processings of coals¹⁻², oil-shale³⁻⁴ and natural gas⁵⁻⁶. The works on application of solar

energy to refining of heavy petroleum fractions are absent.

Instrumentations

The instrument for investigations of solar-thermal pyrolysis and gasification of fuel-oil consists of 1- concentrator for solar radiation, 2- helioreactor, 3- vessel for fuel-oil, 4- vessel for water, 5- evaporator, 6- receiver for liquid products, 7- gasometer, 8- control equipment, 9- chromatography is shown in the scheme diagram fig.1. The petroleum fraction with boiling temperature $T>300^\circ\text{C}$ and middle molecular mass $M=290$, $\rho=0.927\text{ gram per cubic centimeter}$, $\eta=10.3\text{ cSt}$, $n_d=1.474$, the elementary composition (mass: C-87.6, H-11.5, O-0.06, S-0.8, N-0.09) was used as a object solar concentrator with diameter 1.5m, reflection coefficient of mirror surface is 0.8, focal distance-0.6m was used. The power shooting concentrated solar radiation was 1.15kw. Solar radiation reflected

from concentrator is focused on the bottom of helioreactor, which have double wall. Tin was heated up to temperature 500-1200°C. Fuel-oil heated preliminary is given to reaction vessel by dosator and in result of heat action of solar energy chemical reactions proceed. Liquid products of processes are accumulated in receiver and gases are given to gas chromatography.

Mathematical Method

In indicated conditions calorific values of initial fuel-oil (fo) and gaseous products (g) of reaction are $Q_{fo}=4000\text{kJ/h}$, $Q_g=7953\text{kJ/h}$. The value of accumulated solar energy is:

$$Q_{se} = Q_{prod} - Q_{fo} = Q_g - Q_{fo} = 961 \text{ kJ/h}$$

The coefficient of solar energy accumulation at the thermochemical decomposition of fuel-oil is:

$$\eta = Q_{se} / Q_o = Q_{se} / J_o p_s = 0.43$$

Q_{se} – Solar energy flow into reactor,

J_o – intensity of direct solar radiation,

The energy efficiency of processes equals

$$\eta = \frac{\sum Q_{Prod}}{Q_{fo} + Q_o} = 0.77$$

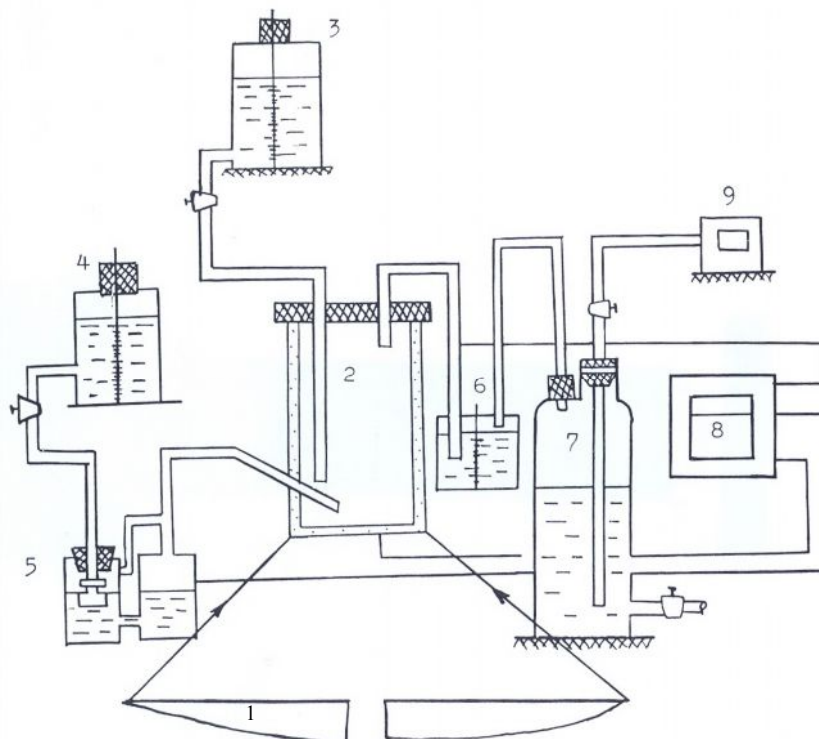


Fig.1. The scheme of experimental plant.

Table 1. Content of gaseous products. Pyrolysis (p), gasification (g)

Temp.°C	500		600		700		800		900		1000	
	p	g	p	g	p	g	p	g	p	g	p	g
H ₂	15	-	18	15.5	20	16.5	23	29	-	22	-	23
CH ₄	31	-	33.5	29	35	27	37	19	-	28.5	-	30
C ₂ H ₄	15	-	19	19.3	23	21.2	21.1	24	-	24	-	23
C ₂ H ₆	6.5	-	9	8.8	6	7	5.3	4	-	3.8	-	3.6
C ₃ H ₆	13	-	12.1	8.1	8.4	9	7.2	8.6	-	5.5	-	3.5
C ₃ H ₈	3	-	1.8	9.4	1.1	8.1	4	4.3	-	4.4	-	3.8
C ₄ H ₈	5.1	-	2.1	-	1.7	-	1.6	-	-	-	-	-
CO	4	-	1.6	8.3	1.1	8.5	1.5	9	-	10.5	-	11

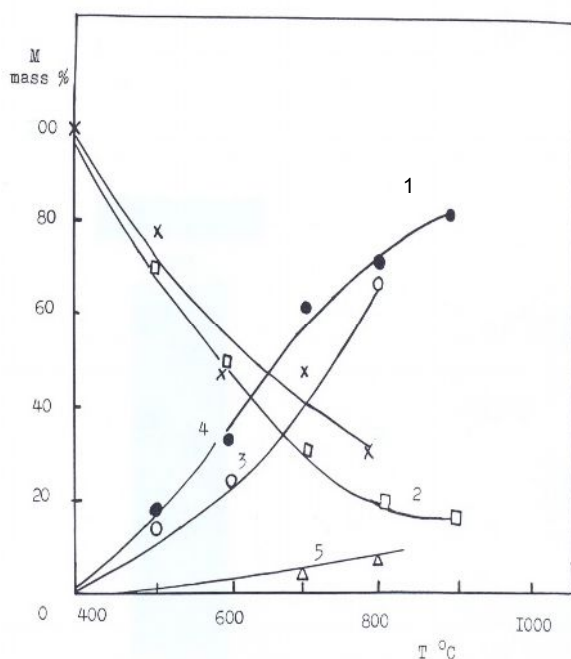


Fig.2. TeperatureversesVS mass%.

Table 2. Content and calorific values of gases at 3 sec.

Gases	Pyrolysis Mass %	Calorific values kJ	Gasification Mass %	Calorific values kJ
H ₂	2.5	335	1.9	250
CH ₄	30	1533	21	1255
C ₂ H ₆	7.8	374	6	317
C ₂ H ₄	31	1460	31.9	1510
C ₃ H ₈	2.2	100	9	477
C ₃ H ₆	16	697	17.6	781
C ₄ H ₁₀	2.4	108	-	-
C ₄ H ₈	4.4	223	-	-
CO	20	20	12	113
	100	4864	100	4705

Results & Discussion

At pyrolysis of fuel-oil gas formation and coke deposit T>600°C are observed. The temperature dependence of fuel-oil decomposition and gas-formation processes are indicated in fig.2. The gas content, formed at pyrolysis is presented in table 1. Activation energy, determined on temperature dependence is E=250kJ/mole. At the investigated limites of contact time and temperature the maximal degree of conversions of fuel-oil was 65% mass (in pyrolysis) and 84% mass (in gasification). The rest of fuel-oil is converted to more heavy products and to coke (up to 7%) in case of pyrolysis. The yield of low molecular olefins hydrocarbon depends extremely on

temperature and contact time. More high summary yields of gases C₂H₄, C₃H₆ & C₄H₈ correspond to temperature 700°C (fig.3) 40% vol., & 55% mass. Such dependence is result of competition processes of dehydrogenation, destruction and polymerization of heavy petroleum fractions.

It follows from presented results that at relative low degree conversions (smaller than 650°C) yield of gasification products lightly differ from pyrolysis products. In case of conversion degree of fuel-oil exceeds 35% contribution of gasification reactions increases. The comparative data on gas formation processes at pyrolysis and gasification of fuel-oil at T=800°C and contact time 3 sec are adduced in table 2

produced at pyrolysis and gasification processes differ 2-3%. Probably only at the high conversion degree of fuel-oil valuable difference in products of these processes may be observed. On the basis of obtained result of some kinetic, thermodynamic and technique-economic aspects of solar-thermal conversions of petroleum residues were analysis. It was established that the rate of thermal generation of radicals in temperature range 600-950°C is $W=3 \times 10^{11} - 3 \times 10^{16}$ radical/sec, but formation rate of products, (methane equals $W=2 \times 10^{13} - 2 \times 10^{17}$ molec/sec.

At more high depth degree the processes become energy-consuming because of exhaustion of light portion of organic compounds in petroleum residues content.

For the case of solar-thermal pyrolysis of fuel-oil at temperature 700°C energy consumption of fuel-gas production was determined. It is evidently from experiment data that at solar energy power $Q=1.15$ kw

gas formation rate is $W=0.6$ m³/h, respectively $\varepsilon=Q/W=1.9$ kw h/m³.

Conclusion

The conversion degree of fuel-oil in gases makes up 65% mass at pyrolysis and 84% mass at gasification of fuel-oil on heliochemical plant. Content of hydrogen in the gaseous products reaches 20% volumes, olefin carbohydrog -40% volume coefficient of power efficiency of processes reaches 67%. It has been shown that specific solar heat power expenditures for gas formation do not exceed 2 kw h/m³. In this case about 30% of potential energy of combust able gases represents accumulated part of solar energy.

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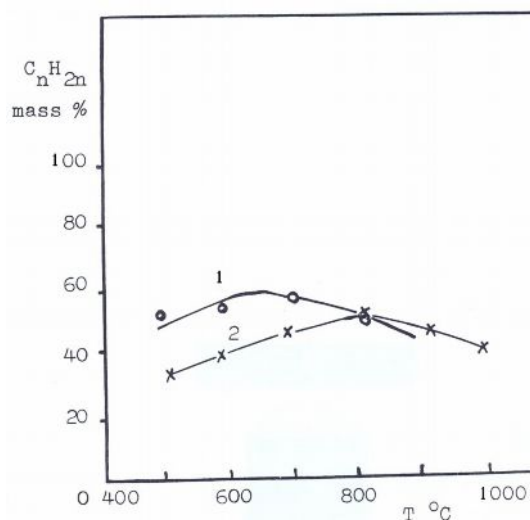


Fig.3. The temperature dependence of mass of olefin hydrocarbons

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