

The average rate of feeding the charge to the furnace was 15 kg. per hr., ranging between 10 and 20 kg. per hr. The best reductions were obtained when the furnace was kept well filled with the charge.

The material used was finely pulverized barytes (98+ per cent BaSO_4) (material used in paints by W. P. Fuller Co.), as large quantities of the precipitated barium sulfate could not be obtained. Six tests were made using city gas and one using oil for fuel. The main object in these tests was to obtain a high reduction of the barium to the water-soluble sulfide; high efficiency of the reducing agent was a secondary consideration. One test (5-7) below, however, was conducted for the purpose of obtaining a higher fuel efficiency than the others. This test showed that almost as high a reduction could be obtained with much less fuel consumption. None of these tests furnished conclusive data for calculating the fuel that would be required for effective reduction in a commercial sized kiln.

TABLE VII—REDUCTION OF COMMERCIAL PULVERIZED BARYTES IN CEMENT KILN

CHARACTER OF C USED	Pulverized Coke		Pulverized Charcoal		None	Pulv. Coke	Coke
TEST NO.	5-1	5-2	5-3	5-4	5-5	5-6	5-7
Per cent C to BaSO_4 in charge	20	15	20	16	0	18	13
Rate Charge: Kg. per hr.	10	10	15	15.2	12.5	16	18.7
Gas Consumption, Cu. ft. per min.	5.4	5.6	6.1	6.3	6.2	oil(a)	3.8
Duration of Test, Total hrs.	25	10	5	5	4	2	4
Av. Temp. ($^{\circ}\text{C}$): Exit Gases	450	460	420	400	510	...	370
Av. Temp. Middle of Kiln	850	880	880	860	900	...	840
Max. Temp. in Kiln (approx.)	1050	1050	1100	1050	1100+	1360	1050
Av. per cent CO in Furnace Gases (middle)	3.8	4.2	3.1	4.2	6.2	...	1.5
ANALYSES OF PRODUCT OF TEST:					(b)		
Per cent of Total Ba:							
Water-soluble	89	87	90	89	69	84	82
Acid-soluble	98	97	98	98	78	96	90
Insoluble (BaSO_4)	2	3	2	2	22	4	10

(a) Product of Test 5-5. Clinkered and unreduced BaSO_4 left in interior of the clinker.

(b) Rate of oil consumption, 3 gals. per hr.

SUMMARY

I—The data obtained in the five series of reduction tests outlined above indicate that the maximum reduction of barium sulfate to sulfide was obtained at the higher temperature, *i. e.*, around 1000°C ., and when the reductions were effected in an indirect fired furnace, *e. g.*, in the muffle furnace, 15 or 16 per cent carbon gave the highest fuel efficiency consistent with completeness of reduction of the barium to the sulfide.

II—In reductions effected in a direct fired furnace (a cement kiln, multiple hearth roasting furnace, or a shaft furnace where hydrogen, hydrocarbons, or where the products of combustion of the fuel, water and carbon dioxide, were brought into contact with the sulfate or sulfide) there were formed a larger proportion of barium compounds insoluble in water, than were formed in a furnace indirectly fired. Thus, although the barium compounds in the best products from a direct fired furnace were 90 to 95 per cent soluble in acid, yet the barium present as the water-soluble sulfide was not more than 85 to 87 per cent of the total.

III—By effecting the reductions rapidly at high temperatures, *i. e.*, above 1000°C ., the proportion

of these water-insoluble barium oxides and carbonates was less than that formed in reductions at lower temperatures over a longer period of time.

IV—Below 750°C . the reduction by carbon or reducing gases was too slow to be considered commercial.

BUREAU OF MINES, WASHINGTON

THE THERMAL DECOMPOSITION OF THE ETHANE-PROPANE FRACTION FROM NATURAL GAS CONDENSATE

By J. E. ZANETTI AND E. H. LESLIE

Received August 3, 1916

In a previous paper¹ one of us presented the results obtained by the thermal decomposition of the propane-butane fraction from natural gas condensate. As a continuation of that work it seemed desirable to study the lower fraction, that containing chiefly ethane and propane, which fraction can likewise be found on the market and is used mainly for lighting and oxygen welding. This fraction comes in cylinders under 500 to 1000 lbs. pressure, and owing to the great difference in boiling points between ethane and butane, -93 and $+1^{\circ}$, is little contaminated by butane. At 750 lbs. and the temperature of 25° the vapor pressure of butane as calculated from Burrell and Robertson's formula²

$\log P = -1633/T + 1.75 \log T - 0.01094 T + 7.590$ is 1545 mm., a little above 2 atmospheres. Since the pressure in the cylinder used was 750 lbs. above atmospheric, at 25° the amount of butane present in the issuing gas would be about 4 per cent. If we consider that the vapor pressure of the butane must be considerably diminished by the fact that it is dissolved in the liquid ethane and propane, the amount of impurity in the gas from this source becomes small. The very high pressure in some of these cylinders would indicate that there is also some dissolved methane in the liquid ethane. The critical temperature for ethane is $+34^{\circ}$ and the critical pressure 50.2 atmospheres. As at 25° the pressures are often above the critical, the only other hydrocarbon present would be methane. This matter is dwelt on at present as it further bears out the observation made by one of us in connection with the propane-butane fraction that the aromatic hydrocarbons obtained from these fractions are built up from aliphatic compounds of lower carbon content than benzene. There is no possibility of aromatics having been obtained here by the splitting off of the benzene ring from phenyl paraffins as no such compound is known that would boil at the temperature of liquid ethane, under atmospheric pressure, or conversely under the pressure of liquid ethane at ordinary temperature. If such compound were present in this gas its vapor pressure would be so small in comparison with that of ethane and propane that it would constitute but a minimal fraction of the issuing gas and it could in no way account for the yield of tar obtained in these experiments—2.5 cc. of tar

¹ THIS JOURNAL, 8 (1916), 674.

² J. Am. Chem. Soc., 37, 2190.

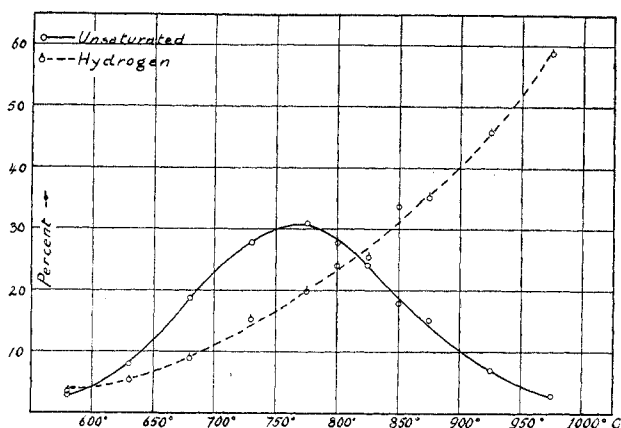


FIG. I—DECOMPOSITION OF ETHANE-PROPANE MIXTURE
NO CATALYZER

(liquid) per cu. ft. of gas used. The cylinder of gas used showed a pressure of 750 at 25° which pressure remained constant, within the limits of accuracy of the gauge used, during these experiments. Analysis of the gas showed it to be composed chiefly of ethane and propane. No CO_2 was present and only less than 0.5 per cent "unsaturated."

The apparatus and method of procedure were exactly as described in the case of the propane-butane fraction. The gas was passed at a measured rate through a heating chamber, the tar "fog" formed precipitated electrically and samples of the gas analyzed for "unsaturated" and hydrogen. The results of these analyses are plotted in Fig. I. As in the case of the butane-propane fraction, the percentage of "unsaturated" increases gradually to a maximum in the neighborhood of 750°, decreasing again above that temperature to a minimum at about 950°. The content of hydrogen increases slowly at first, a marked increase in its rate taking place above 750°. The beginning of the decrease in "unsaturated" formation and of the increase in hydrogen formation are coincident, as noted in the case of the propane-butane fraction with the appearance of the tar "fog."

The "unsaturated," as shown by fractionation of the bromides, consisted chiefly of ethylene and propylene with small amounts of butene. The presence of butenes, which occurred in a very small amount, is doubtless due to the decomposition of the butanes, which, as pointed out above, must occur in the gas in small amounts.

The tar formation occurred at about 750°. The yield was very much smaller than in the case of the butane-propane fraction, amounting to only 2.5 cc. per cu. ft. of gas used. This might be expected from the fact that the average molar weight of the gas is much smaller than in the other fraction. How much of this aromatic formation is contributed by the ethane and how much by the propane is a question which we cannot discuss at the present moment. That the ethane does contribute to some extent can not be doubted since Bone and Coward¹ have found it to be the case, though only to a slight extent. The very small percentage of the lower boiling aromatics and

¹ *J. Chem. Soc.*, 93, 1197.

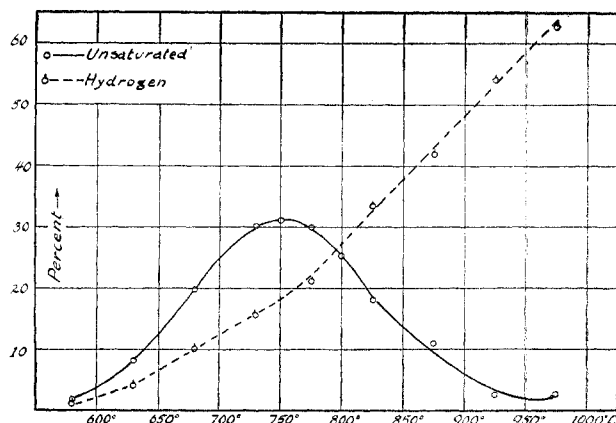


FIG. II—DECOMPOSITION OF ETHANE-PROPANE MIXTURE, USING COPPER
AS CATALYZER

the unusually high one of naphthalene is worthy of notice. Only about 3 cc. out of 20 cc. of tar came over below 125° and about 1 cc. more below 200°. The rest was naphthalene and pitch. The naphthalene formed choked the condenser coil several times during a run and could be noticed in large flakes at the end of the quartz tube when cleaning out the apparatus between experiments.

The effect of copper as catalyzer was not marked in any way. The results when plotted (Fig. II) were, both for the "unsaturated" and for hydrogen, very similar to those obtained without a catalyzer. The aromatic formation proceeded in much the same way.

With iron as catalyzer (Fig. III) the same sharp drop in the unsaturated content at about 710° was noticed as with the propane-butane fraction, the hydrogen content increasing very rapidly as the "unsaturated" decrease. No aromatic formation was noticeable beyond the formation of a slight amount of "fog." Much carbon was deposited on the catalyzer necessitating its frequent renewal.

EXPERIMENTAL

MATERIAL—The material was a "liquid gas" from West Virginia in a steel cylinder under 750 lbs. pressure at 25°. The results of the explosion with oxygen are given in Table I. Analyses I and II were made at the beginning, III and IV at the end of the experiments presented. The gas had in addition 0.4 per cent "unsaturated" and about 0.5 per cent hydrogen. There was no CO_2 .

TABLE I—ANALYSIS OF GAS

ANALYSIS:	I	II	III	IV
Volume gas.....	12.3	12.3	11.7	12.2
Contraction.....	34.4	34.0	32.0	33.9
Volume CO_2	29.9	29.6	30.9	31.7

APPARATUS AND PROCEDURE—The apparatus and procedure were the same in all respects as used for the propane-butane fraction and their description is unnecessary. The rate of gas flow through the chamber was the same, 0.45 cu. ft. per hr.

GAS ANALYSIS—The gas analysis was conducted over water. For the determination of the "unsaturated," bromine was used. The hydrogen was determined by combustion over copper oxide. The results are given in Table II.

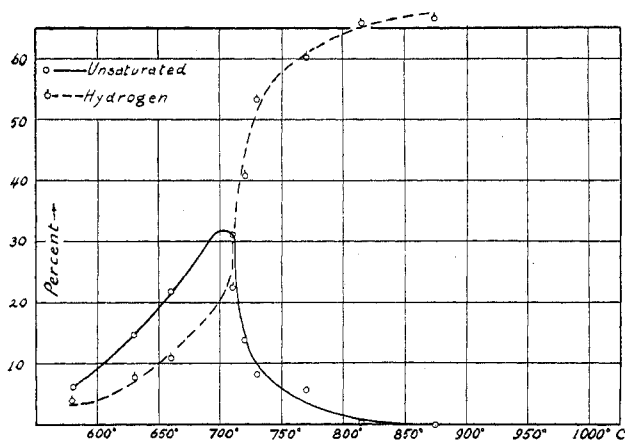


FIG. III—DECOMPOSITION OF ETHANE-PROPANE MIXTURE, USING IRON AS CATALYZER

THE "UNSATURATED"—The gases coming between 800 and 850° were passed into bromine till the latter became colorless. After drying, 25 cc. were distilled and the following fractions collected: 5 cc. below 127°; 9 cc., 127–132°; 5 cc., 132–142°; 5 cc. residue. On allowing the residue to stand a small amount of crystals separated out. Pressing from the mother liquor and crystallizing from alcohol they were obtained in the form of small, transparent, prismatic crystals melting at 116°.

AROMATICS—The tar obtained was quite fluid and after filtering showed a specific gravity of 1.075. Twenty cc. were distilled in a small flask. Three cc. came over below 125°, 1 cc. below 200°. Above that, naphthalene began to solidify in the condenser. The distillation was continued under reduced pressure, about 8 cc. coming over and solidifying to a yellowish

TABLE II—ANALYSIS OF GASEOUS PRODUCTS WITH AND WITHOUT CATALYZER

NO CATALYZER			COPPER AS CATALYZER			IRON AS CATALYZER		
Temp. ° C.	Unsat- urated Per cent	H Per cent	Temp. ° C.	Unsat- urated Per cent	H Per cent	Temp. ° C.	Unsat- urated Per cent	H Per cent
580	2.8	3.4	580	1.7	1.3	580	6.1	3.6
630	7.8	5.8	630	8.1	4.0	630	14.9	7.9
680	18.9	8.8	680	19.9	10.1	660	22.0	10.9
730	28.0	15.3	730	30.2	15.6	710	31.2	22.5
775	31.0	19.6	750	31.5	...	720	14.2	40.9
800	27.9	24.0	775	30.0	21.2	730	8.3	53.4
825	24.2	26.1	800	25.4	...	770	5.7	60.3
850	18.0	34.0	825	18.2	33.5	815	0.3	65.8
875	15.2	35.3	875	11.0	42.0	875	0.0	66.6
925	7.2	46.4	925	2.6	54.0			
975	3.0	58.8	975	2.8	62.7			

mass of crystals. On crystallizing from alcohol they gave a melting point of 79°. The residue solidified in the flask, forming a black pitch with a strong odor resembling anthracene. Nitrobenzole was obtained from the fraction boiling below 125°, but no nitrotoluels could be obtained from it.

SUMMARY

I—It has been shown that mixtures of ethane and propane decompose at high temperatures, giving ethylene, propylene and other "unsaturated," hydrogen and aromatics.

II—The percentage of "unsaturated" increases with increasing temperatures to a maximum in the neighborhood of 750°, then decreases with increasing temperatures. The aromatic formation begins at about 750° C. and is coincident with an increase in the rate of hydrogen formation.

III—The action of copper and iron as catalyzer has been studied. Iron prevents aromatic formation and favors the decomposition of the hydrocarbons into carbon and hydrogen.

Further work upon these topics is now in progress in this laboratory.

DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY
NEW YORK CITY

THE SOLUBILITY OF LEUCITE IN SULFUROUS ACID

By J. SCHROEDER

Received May 19, 1916.

Leucite belongs to a class of potash-carrying silicates that has received considerable attention as a possible source of potash.¹ It is a metasilicate of aluminum and potassium having the formula $KAl(SiO_3)_2$ or $K_2O, Al_2O_3 \cdot 4SiO_2$. On this basis its theoretical composition is: Silica, 55.0 per cent; alumina, 23.5 per cent; and potash, 21.5 per cent. From this it is evident that in potash content it is one of the richest minerals known.

Leucite occurs in the more recent volcanic rocks as embedded crystals, grains, or aggregates of grains. It is identified especially with the lavas of Mt. Vesuvius and other localities in Italy, though its occurrence is by no means restricted to these localities. In North America it is found in Lower California, New Jersey, Arkansas, British Columbia, and especially in several places outlying from the Rocky Mountains, notably the Leucite Hills of Wyoming. These hills are situated in southwestern Wyoming from 10 to 15 miles north of Bitter Creek, which is an eastern tributary of Green River and is followed by the Union Pacific Railroad.

The Leucite Hills consist of a number of conical peaks of lava protruded through the beds of rocks forming the plateau of the surrounding neighborhood. Each peak consists of a lava sheet, presenting an abrupt wall from 50 to 150 ft. high. These deposits are described in detail by Schultz and Cross.²

The leucite rocks of this neighborhood are of a yellowish gray color and often, if not always, of a pronounced cellular structure. The porosity, however, does not reach the pumice stage. The leucite inclusions are microscopic crystals 0.035 mm. in diameter. The chemical composition of the rocks as indicated by the analyses of the United States Geological Survey is about as follows: Silica, 53 per cent; alumina, 11 per cent; ferric oxide, 3 per cent; magnesia, 6.5 per cent; lime, 4.5 per cent; soda, 1.5 per cent; and potash, 11 per cent.²

To ascertain the possibility of recovering this potash by leaching, solubility tests were made with sulfurous acid. A sample of leucite rock from Batuku, Celebes, East Indies, containing 9 per cent potash, was obtained through the courtesy of Dr. J. P. Iddings of the United States National Museum. This was ground and separated, by sifting, into portions of different fineness and these portions shaken over night with a solution of sulfurous acid. The latter was prepared by passing sulfur dioxide through water to approximate satura-

¹ Cushman and Coggeshall, *THIS JOURNAL*, 4 (1912), 821.

² U. S. Geol. Survey, *Bull.* 512.