

LIQUEFACTION OF ESTONIAN KUKERSITE OIL SHALE KEROGEN WITH SELECTED SUPERHEATED SOLVENTS IN STATIC CONDITIONS

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Estonian kukersite oil shale kerogen was liquefied in an autoclave in unified liquefaction conditions in the presence of the following superheated solvents: benzene, diethyl ether, ethanol, n-hexane, dimethyl ketone and water. Different yields of liquid, solid and gaseous products were obtained. Particularly high yields of the liquid product were recorded when some solvents were chemically incorporated into the composition of the kerogen decomposition products. Liquid products soluble in benzene were characterized, irrespective of the solvent used for kerogen liquefaction, by significant content of bituminous fractions, typical constituents of thermobitumen but not typical of kukersite semicoking oil. Concentration of compounds separable by chromatographic methods, in particular, that of n-alkanes, alkenes, polycyclic aromatic hydrocarbons and phenols present in abundance in the composition of semicoking oil, is low. Contra versa to semicoking oil, long hydrocarbon chains C₁₇ to C₂₄ prevail over short C₅ to C₁₂ ones. Extent of kerogen and thermobitumen decomposition strongly depends on the type of solvent used for liquefaction. Both process efficiency and selectivity can be noticeably influenced by solvent selection, and not only thermosolvolytically but also chemically modified products can be produced.

Introduction

Superheated and supercritical solvents, mainly water and aqueous solutions, have been effectively used in thermal decomposition and chemical transformation of a wide range of complicated organic molecules in areas as diverse as recycling of polymeric wastes, synthesis of chemicals, and generation of liquid fuels from both natural and technological source materials [1–6]. Thermal debituminization of the fossilized organic matter of kerogen and kerogen-like formations can also be significantly accelerated in

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the presence of solvents, and not only water but many other solvents can be successfully used in thermosolvolytical extraction and thermochemical conversion processes of fossilized and renewable high-molecular organic matter [7–12].

It has been presumed that even high-molecular compounds can be dissolved in superheated solvents thanks to high phase density (up to 300 kg/m³). Being diluted the products formed contact and interact passively at relatively low temperatures. Yields of the liquid (benzene-soluble) product as high as at Fischer assay retorting are obtained by liquefaction in the presence of superheated solvent in an autoclave at temperatures lower by 150–170 °C. Even much higher yield of solubles can be achieved if a reasonable compromise between process variables (temperature, pressure, time, solvent-to-kerogen ratio) has been found [13].

Only the presence of solvent itself and physical parameters used to realize the liquefaction do not determine the process efficiency and selectivity. In addition to the former ones just the type of solvent, its chemical composition and thermosolvolytical properties strongly effect the process. Multilateral interactions between solvent, kerogen and its decomposition products have not been thoroughly investigated. Bilateral interactions occurring between superheated solvent and thermobitumen have not been elucidated at all. Explanations are needed to understand the effects of solvent type, as well as efficiencies and selectivities of various superheated solvents have to be estimated. Superdense medium as conservator was thought to avoid further decomposition of high-molecular mass compounds dissolved in it. Though, one can assume that secondary destructive processes occur in superheated medium, too; those are decelerated. Under severe liquefaction conditions or using special solvents, liquefaction of kerogen can presumably result in both kerogen thermobituminization and thermobitumen decomposition into secondary shale oil.

The goal of the current study was to investigate the effect of solvent type on the yield and composition of Estonian kukersite oil shale kerogen liquefaction products in order to maximize the yield of the liquid product and to elucidate alterations in its composition concurring with the use of different solvents. Unified static liquefaction conditions were employed to obtain comparable data, and individual solvents belonging to different chemical compound classes, such as aliphatic and aromatic hydrocarbons, alcohols, ketones, ethers and water as most common and available one, were used.

Experimental

The model sample used was enriched kerogen of kukersite containing 72.4% organic matter (kerogen-70).

Benzene, diethyl ether, ethanol, *n*-hexane, dimethyl ketone and water were used as solvents at liquefaction of kerogen-70.

For liquefaction tests a 500-cm³ rocking autoclave charged with a powdered kerogen sample and solvent was used. Static liquefaction conditions of all experiments were unified as follows: temperature 360 °C, time 4 h, sample-to-solvent ratio (wt.%) 1 : 3 (40 g : 120 g). The temperature was raised to a fixed level during 0.5 h, and the time was measured as soon as 360 °C was reached. At the end of heating the system was cooled down to room temperature, autoclave valve was opened and volatile at room temperature compounds were collected as gas.

Liquid and solid products remaining in the autoclave were diluted with benzene, and the liquid products were separated from solid ones by filtration. The yield of liquid was determined as the amount of benzene-soluble compounds. Liquefaction solvent and benzene were removed by two-stage rotary evaporation. Chemical composition of the benzene-solubles was investigated using infrared spectroscopic (Specord 75IR) and chromatographic techniques as follows: benzene-solubles were separated into the groups of compounds by preparative thin layer chromatography (TLC).

Plates 24 × 24 cm coated with a 2-mm silica gel (40 µm) layer were used, and 0.5 g samples were analyzed. *n*-Hexane was used as eluent and the content of each eluted compound group (non-aromatic hydrocarbons, mono- and polyaromatic hydrocarbons and heteroatomic compounds) was determined. Phenols were extracted from the liquid products with 10% sodium hydroxide. The content of asphaltenes in benzene-solubles was determined as the share of insoluble in *n*-hexane compounds. The volatiles and TLC fractions were analyzed by temperature-programmed gas chromatography (Chrom-5) in columns of different polarity.

Results and Discussion

Efficiency Studies

Yields of liquid, solid and gaseous products obtained are given in Table 1.

Table 1. Yield of Liquefaction Products, Mass%, on Kerogen Concentrate Organic Matter Basis

No.	Solvent	Products*		
		Liquid	Gas	Solid
1	Benzene	81.5	3.5	13.4
2	Diethyl ether	106.3	134.9	0.1
3	Ethanol	99.0	27.6	0.5
4	<i>n</i> -Hexane	72.8	8.6	16.7
5	Dimethyl ketone	145.7	19.3	0.3
6	Water	69.6	14.5	16.0

* The yields of single products were determined by direct weighting, the sum differs from 100% due to losses, and the share of solvent is not taken into account in calculation.

One can see (Table 1) that high and exceptionally high in several cases yields of liquid and gaseous products were obtained, surpassing the total liquid or gas generation potential of kerogen. The yield of liquid product was in all cases, irrespective of solvent used, higher than that at semicoking (66%), being 69–145%, on basis of organic matter weighted into the autoclave. Gas yields calculated by the same way vary in a large range – 4–135%.

The data in Table 1 refer to a very marked effect of not only solvent's solvolytical power but just its stability qualities and chemical activity towards kerogen and kerogen liquefaction products during the liquefaction process. Data in Table 2 demonstrate that some of the solvents used decompose, and being decomposed forming chemically active fragments, the latter begin to react with kerogen and kerogen fragmentation products incorporating into liquid, gaseous and even solid products finally formed. So, chemically modified final products can be obtained depending on the type of superheated solvent used. The results of solvent transformations also investigated in this work are presented in Table 2.

Table 2. Gas Yield, on (Kerogen Concentrate Organic Matter + Solvent) Basis, and Solvent Recovery, Mass%

Superheated solvent			Gas
Used (120 g = 100%)	Recovered	Transformed*	
Benzene	99.5	–	0.7
Diethyl ether	52.1	0.4	26.4
Ethanol	74.0	1.7	5.4
<i>n</i> -Hexane	98.2	–	1.7
Dimethyl ketone	72.9	–	3.8
Water	100.2	–	2.8

* Liquids insoluble in parent solvent were determined.

Solvents used are partially or completely soluble mutually and with transformed ones. Besides, diethyl ether, *n*-hexane and dimethyl ketone are volatile at room temperature already. Being blended and repeatedly submitted to evaporation, condensation and other chemical separation techniques causing losses at every stage, the amounts of solvents recovered or transformed given in Table 2 are not too reliable for precise material balances, but urgently needed to give insight into general tendencies. Basing on the data in Tables 1 and 2, hydrocarbon-type solvents as benzene and *n*-hexane seem to maintain their stability and inertia even at superheated state and do not react with kerogen structural elements. After evaporation those solvents are recovered as benzene or *n*-hexane only. Differences in the liquid product and gas yields have been caused by differing solvolytical and destructive power of superheated benzene and *n*-hexane under the conditions created.

In this work benzene was used as the solvent for separation of liquid products and also as one of the superheated solvents. To compare solvolytical efficiency of benzene with other superheated solvents, the benzene-soluble liquid product was dissolved once more at room temperature in the solvent used at kerogen liquefaction (see Table 3).

Table 3. Solubility of Benzene-Soluble Liquid Products in the Parent Superheated Solvent Used at Liquefaction in Its State

No.	Superheated solvent used at liquefaction	Solubility in the parent solvent, mass %
1	Benzene	100.0
2	Diethyl ether	57.3
3	Ethanol	31.7
4	<i>n</i> -Hexane	55.0
5	Dimethyl ketone	77.6
6	Water	12.2

The data in Table 3 indicate that the solubility of liquid products in the solvents used at their formation during thermosolvolytical liquefaction is incomplete varying between 12.2–77.6%, being lowest for water and highest for dimethyl ketone. The similar regularities can be observed in Table 1. The most unexpected results concerning benzene-soluble liquid products are their poor solubility in ethanol, and, in particular, high yield of hydrophilic compounds obtained at liquefaction with superheated water. The content of water-soluble acids and alkalis in kukersite shale oil, hydrogenisate or thermal dissolution oils is usually low, and mainly water-soluble phenols are presented.

Data in Tables 1 and 3 demonstrate that benzene, compared with other solvents used, is actually an extra-effective solvent to remove liquid products obtained at kukersite kerogen liquefaction from the solid residue.

Selectivity Studies

Functional Groups

Infrared spectra of the liquid benzene-soluble products are presented in Fig. 1. One can see that spectra obtained in the medium of solvents stable and chemically inert under superheated conditions (benzene, *n*-hexane, water) are similar and noticeably differ from the spectra recorded when labile and chemically active solvents (diethyl ether, ethanol, dimethyl ketone) were used.

All spectra have common absorption bands at 725, 750, 1380, 1460, 2860, 2930 and 2960 cm^{-1} , and at 745, 770, 820, 880, 1020, 1080, 1600, and about 3000 cm^{-1} indicating, respectively, the presence of CH_3 -, $-\text{CH}_2$ - and

CH- groups in aliphatic chains and aromatic ring systems of different degree of condensation and substitution. Broad absorption bands with a maximum at $3450\text{--}3500\text{ cm}^{-1}$ indicating various OH groups and absorption at $1700\text{--}1720\text{ cm}^{-1}$ belonging to the C=O groups are common, too.

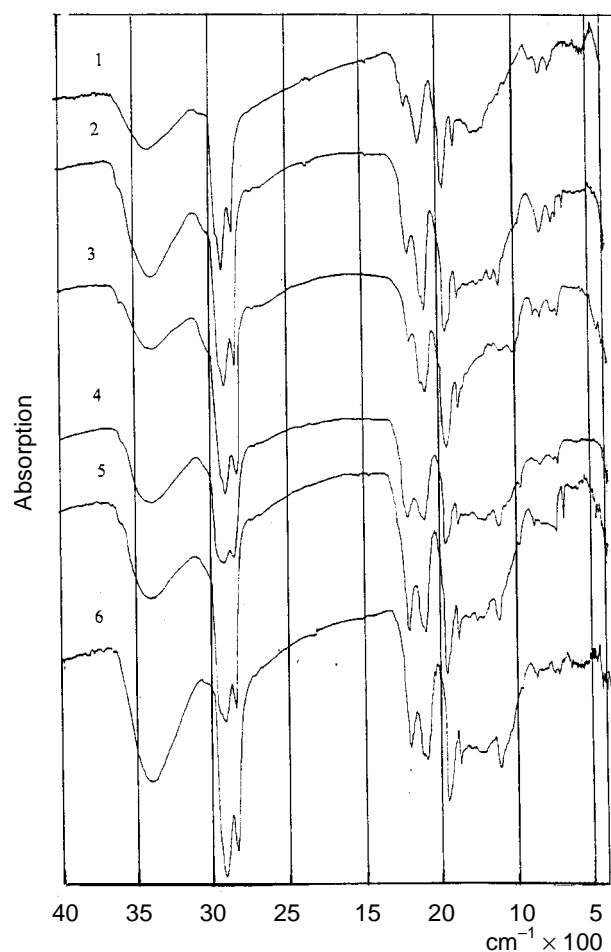


Fig. 1. Infrared spectra of liquid products obtained on kukersite kerogen liquefaction in following superheated solvents: benzene(1), *n*-hexane (2), water (3), ethanol (4), diethyl ether(5), dimethyl ketone (6)

Besides those groups there are some other absorptions indicating specific effects caused by the action of chemically active solvents. Absorptions at $2990\text{--}2970$, 2850 , 1430 and $1300\text{--}1100\text{ cm}^{-1}$ originate from C–O and C–O–C and C=O groups incorporated from diethyl ether and dimethyl ketone. Also absorption at 1720 cm^{-1} , belonging to the C=O groups in dimethyl ketone and diethyl ether liquids, is considerably amplified as compared with that in other liquid products. In the case of ethanol liquid one can notice an

increase in absorptions at 2930 and 2960 cm^{-1} and appearance of narrow absorption at nearby 1740 cm^{-1} , the former absorptions belonging to methylene and terminal methyl groups in mainly cycloalkanes and aliphatic heterocompounds, and the latter one being a result of incorporation of acetaldehyde into the liquid product composition.

Group and Componental Composition

Gas composition is characterized in Table 4.

Table 4. The Main Gaseous Components Formed at Liquefaction of Kukersite Kerogen, Vol. %

Component	Superheated solvent used at liquefaction					
	Benzene	Diethyl ether	Ethanol	<i>n</i> -Hexane	Dimethyl ketone	Water
Hydrogen	5.9	0.9	0.1	5.6	2.6	9.8
Carbon monoxide	12.3	16.3	11.2	9.8	19.0	–
Carbon dioxide	20.2	9.7	15.7	22.5	23.0	27.5
Methane	25.8	25.3	31.6	23.0	38.6	18.0
C ₂ –C ₄ alkanes	10.5	42.4*	29.3**	12.7	9.7	14.1
C ₂ –C ₄ alkenes	0.9	1.3	6.5	1.3	1.2	0.8

* Ethane content 99.5%

** Ethane content 92.2%.

Discussing the data in Table 4 one can find the following. As expected, gas formed in the presence of chemically stable C₆-hydrocarbons and water is of similar composition, and strongly differs from that obtained in the presence of unstable and chemically active solvents. Liquefaction of kerogen in both hydrocarbon and aqueous superheated solvents yielded only kerogen-derived gaseous components while gas produced in superheated diethyl ether, ethanol or dimethyl ketone consisted mainly of thermal and thermochemical decomposition products of the solvents.

Gases, particularly those obtained using reactive solvents, were rich in alkanes C₁–C₄, whose yield reached even 60–67%. Considerable amounts of both carbon oxides and methane were yielded (26–32 vol.%), but their maximum yields, 42 and 39 vol.%, respectively, were produced in the case of dimethyl ketone decomposition. Outstandingly high is the share of ethane among saturated C₂–C₄ hydrocarbons, reaching 92–99% when superheated ether and alcohol were used. The content of unsaturated hydrocarbons C₂–C₄ is extremely low (0.9–1.3 vol.%) in all cases except ethanol (6.5 vol.%). One can suppose that decomposition of diethyl ether and ethanol both resulted in abundant formation of ethylene radicals which can stabilize reacting with active hydrogen from the same solvent decomposition and, in addition, with hydrogen from kerogen decomposition, forming ethane and other saturated hydrocarbons. Low content of both hydrogen and unsaturated hydrocarbons in gas indicate active consumption of hydrogen formed during kerogen destruction reactions.

Group composition of liquid products is presented in Table 5.

Table 5. Chemical Group Composition of Liquid Benzene-Soluble Products (Mass%) Obtained Using Various Superheated Solvents at 360 °C

Solvent	Compound groups						
	Asphaltenes	High polar heteroatomic malthenes	Oxygen compounds		Hydrocarbons		
			Neutral	Acidic	Aromatic		Aliphatic
					Polycyclic	Monocyclic	
Benzene	45.6	23.7	10.4	1.4	10.3	2.4	6.2
Diethyl ether	48.8	21.4	10.0	3.2	8.8	0.4	7.4
Ethanol	36.1	31.2	10.8	1.9	9.5	2.7	7.8
<i>n</i> -Hexane	45.0	24.7	8.4	1.4	11.3	2.0	7.2
Dimethyl ketone	31.0	22.2	23.5	4.0	10.9	2.9	5.6
Water	37.3	36.2	7.0	4.7	2.7	1.3	10.8

Irrespective of solvent used the benzene-soluble compounds separated are characterized by very little flowability in normal conditions and low volatility both caused by high content of bituminous fractions – asphaltenes and high-polar heteroatomic malthenes – the constituents forming almost 70% of the total liquid. The highest content of bituminous fractions was fixed in the liquid product obtained in aqueous medium (73.5%), but exceptionally low content of those fractions was found in the product obtained in dimethyl ketone (53.2% only). By physical and chemical qualities and chemical composition, the liquid products obtained are similar to thermobitumen – the primary product of kukersite kerogen pyrolytical decomposition, whose formation begins at 250 °C already, and whose decomposition is observable over 350 °C [14–16].

As the main part of shale oil forms not directly from kerogen but as a result of thermobitumen decomposition, one can, basing on the data in Table 5, deduce that both thermobitumen and oil formation are significantly accelerated in the presence of superheated solvents. Depending on the type of solvent used the velocities of not only thermobitumen formation but also of its decomposition (oil formation) differ determining solvent efficiency. Asphaltenes and a part of malthenes, high polar high-molecular bituminous components similar to those in thermobitumen, are characterized as primary fragments of not completely decomposed kerogen and, being susceptible to temperature and solvent action, yield secondary products typical of semicoking oil on further decomposition.

The latters belong to less- or non-polar malthenes and are aliphatic and aromatic hydrocarbons, neutral oxygen compounds and phenols. So, the higher the ratio of malthenes-to-bituminous fractions, the higher the decomposition degree of thermobitumen, and the higher thermosolvolytical

destruction power of the solvent towards both kerogen and thermobitumen, resulting in oil formation. In this context the solvents used can be arranged by their destructive power towards kerogen as follows:

Dimethyl ketone (0.88) > ethanol (0.49) > benzene (0.44) > *n*-hexane (0.43) > diethyl ether (0.42) > water (0.36).

At making such arrangement the yield of liquid product as the main parameter characterizing thermosolvolytical power of the solvents used was not taken into account. Comparing the data calculated on liquid product qualitative composition with liquid product quantitative yields obtained experimentally (see Table 1), one can see that solvents' arrangement is the same except for diethyl ether that has been replaced from the second position to the last but one. For a more adequate estimation of the solvent role the following additional factors should be considered: thermobitumen formation/decomposition and oil formation can be partly simultaneous but not permanently consequent reactions, solvent can chemically affect the yield of thermobitumen and its decomposition products and, last but not least, the end point of thermobitumen formation is not the same when different solvents are used.

The regularities demonstrated in Table 1 (solvent action on kerogen) and above (solvent action on kerogen-derived thermobitumen) confirm the suspicions that solvent attacks not only kerogen but, subsequently, high-molecular fragments in thermobitumen formed from kerogen. Thermobitumen decomposition degree depends on both pyrolysis temperature and time. In this work these parameters were unified –360 °C and 4 h in all experiments, but different solvents in equal quantities were added resulting, nevertheless, in individual and different decomposition degree of thermobitumen.

The regularity indicates that the different solvents act differently. Discussing the data in Table 5 one can assert that thermobitumen having been formed in almost to maximum yields, was not subjected to significant conversion. The total yield of asphaltenes and high-polar heteroatomic malthenes as thermobitumen constituents, measured in most cases 67–74%, indicates that thermobitumen decomposition had not been complete in the experimental conditions used. That fact is confirmed by low content of phenols (1–5% only), being usually 25% in semicoking oil which is a thermobitumen decomposition product as well. Low phenol content of liquid benzene-soluble products obtained indicates that phenols form in final stages of thermobitumen decomposition.

The content of neutral oxygen compounds and hydrocarbons did not achieve even a half of that present in semicoking oil (except liquid product obtained in superheated dimethyl ketone medium) indicating their sufficient reserve in nondecomposed thermobitumen. Using gas-chromatographic techniques, besides neutral oxygen compounds (alkanones), alkylarenes and *n*-alkanes were determined, whose aliphatic (side) chains contained up to 17–24 carbon atoms. The concentration of longer chains is lower, and that of

short chains (up to C₁₂) is negligible. Though a part of lighter hydrocarbons can get lost during benzene evaporation, one can say, basing on this fact and taking into account low gas yields, that cracking reactions play small role at thermobitumen decomposition under conditions used.

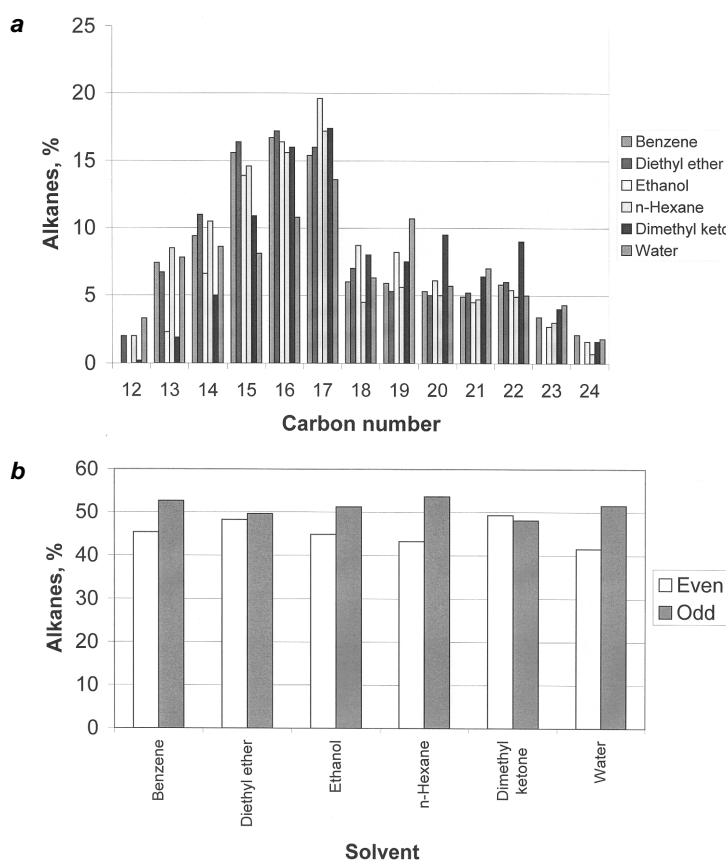


Fig. 2. Relative concentrations of *n*-alkanes separated by thin-layer chromatography and determined by gas chromatography: *a*-individual compounds, *b*-summarized even- and odd-numbered homologues separately

n-Alkanes separated by thin-layer chromatography were submitted to additional investigation, and concentrations of individual homologues in all liquid products obtained were determined (see Fig. 2). One can notice that though odd-numbered chains dominate over even-numbered ones, a fact typical of kukersite kerogen destruction products, the distribution of individual compounds by chain length depends on the solvent used, and that is different for each single solvent. The prevalence of odd-numbered alkanes is particularly noticeable in the case when benzene, *n*-hexane and water, chemically inert at liquefaction conditions, were used. Other solvents, especially diethyl ether and dimethyl ketone produce, thanks to their

chemical effects, both odd- and even-numbered homologous in practically equal quantities. As the extent of kerogen debituminization was high and that of thermobitumen decomposition low, in liquid benzene-soluble products also the maximums at C₁₆ and C₁₇ are unlooked-for kukersite kerogen destruction products; significantly higher concentrations of C₁₈–C₂₄ and extremely low ones of C₅–C₁₂ were recorded compared with kukersite semicoking oil.

Summing up the investigation results: high yields of liquid products of predicted or modified chemical composition can be obtained both on kerogen basis or on account of expropriated part from the solvent selected to create respective superheated conditions.

Conclusions

Special characteristics of individual superheated solvents can significantly influence both the process efficiency and kerogen liquefaction selectivity. High-molecular primary fragments from kerogen debituminization are rather submitted to further conversion than dissolved and retained in superheated surroundings.

The yield of liquid product and its composition can significantly differ when using various individual solvents under unified conditions, but at the same time comparable yields of liquid product of similar or modified chemical composition can be obtained at altering the process variables by changing the solvent.

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