BIOMASS FLASH PYROLYSIS EXPERIMENTS BETWEEN 1073 K AND 1273 K

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ABSTRACT: Analytical experiments are performed in an entrained flow reactor to better understand the kinetic processes involved in biomass pyrolysis under high temperatures (1073-1273 K) and flash heating condition (>500 $K.s^{-1}$). The influence of the particle size (0.4 and 1.1 mm), of the temperature range (1073-1273 K), of the presence of steam in the gas atmosphere (0 or 20 vol %) and of the residence time range (between 0.7 and 3.5 s for gas) on conversion and selectivity is studied. Under these conditions, the particle size is the most crucial parameter that influences decomposition. For 1.1 mm particles, pyrolysis requires more than 0.5 s and heat transfer processes are limiting. For 0.4 mm particles, pyrolysis seems finished after 0.5 s. More than 70 wt % of gas is produced. 40 % of the initial carbon is found in CO; less than 5% is found in CO_2. The hydrogen content is equally distributed among H_2, H_2O and light hydrocarbons (CH_4, C_2H_2, C_2H_4). Under these conditions, the evolution of the produced gas mixture is not very significant during the first few seconds, even if there seems to be some reactions between H_2, the C_2 and tars.

Keywords: flash pyrolysis, entrained flow reactor, gas yields.

1 INTRODUCTION

The Commissariat à l'Energie Atomique (CEA) has launched a research and development program called Biocarb. This project aims at developing a process that produces synthesis gas (H_2, CO) from thermochemical conversion of biomass with enough purity for liquid fuel synthesis or use in a fuel cell. The process is divided into four main sections:

• Preparation and drying of the biomass
• Steam gasification of biomass into synthesis gas
• Post-treatment of synthesis gas
• Conversion of synthesis gas into liquid fuels through Fischer-Tropsch synthesis.

An important part of the research is focused on the step of biomass steam gasification, and particularly on the understanding of the gasification mechanisms at the particle scale under typical conditions encountered in fluidized bed gasifiers (1073 K<T<1273 K; P=1 bar; heating rate>500 $K.s^{-1}$).

The present work consists in analytical experiments that should help to better understand the processes involved in the first stage of the reaction, namely biomass pyrolysis. Note that in our study, pyrolysis includes both solid decomposition, often called "primary pyrolysis", and the reactions of the vapours produced during primary pyrolysis.

Section 2 is devoted to the description of the experiments. Results are shown and discussed in section 3. Eventually, conclusions are drawn in section 4.

2 DESCRIPTION OF THE EXPERIMENTS

2.1 Biomass samples

The biomass used in this study is a mixture of two softwoods (sylvester pine and spruce). Two particle sizes are considered: 355-530 µm, called 0.4 mm and 1.00-1.25 mm, called 1.1 mm. The data on biomass samples are given in table I.

Table I: Data on biomass samples

	Units	Sample 0.4 mm	Sample 1.1 mm
Carbon	wmaf %[a]	48.6	50.5
Hydrogen	wmaf %	6.0	6.25
Nitrogen	wmaf %	0.2	0.1
Sulfur	wmaf %	0.03	0.02
Oxygen	wmaf %	43.0	43.1
Elemental formula		$C_6H_{8.8}O_{3.9}$	$C_6H_{8.8}O_{4.0}$
Moisture	w %	7.2	8.6
Volatile matter	wmf %[b]	77.0	77.4
Fixed Carbon	wmf %	20.9	21.9
Ash	wmf %	2.1	0.6

[a] wmaf %: mass percent moisture ash free
[b] wmf %: mass percent moisture free

2.2 Experimental facility

The experiments are performed in an Entrained Flow Reactor shown in figure 1. A complete description of the apparatus and its thermal and hydrodynamic characterization are given in previous works [1;2].

The reactor is made up of an alumina tube heated by an electric oven that can reach 1273 K. Feed gas is either pure N_2 or a mixture of 80% N_2 and 20% steam. The gas is injected at the top of the reactor with a flow rate of 16 $L.min^{-1}$(STP) and then passes through an electric preheater. The solid particles are injected at the top of the reactor by pneumatic transport (flow rate of N_2=2 $L.min^{-1}$(STP)) in a tube which is cooled by thermal oil. The solid flow rate is 1 $g.min^{-1}$, which ensures that particles may be assumed to be isolated from each other. A dispersion dome is placed at the outlet of the cooled tube, in order to distribute the particles as homogeneously as possible over the reactor cross-section. Under the explored conditions, flow is laminar (Re<2000). Measurements have shown that the reactor is isothermal in the zone between 0.30 and 0.95 m away from the solid injection.
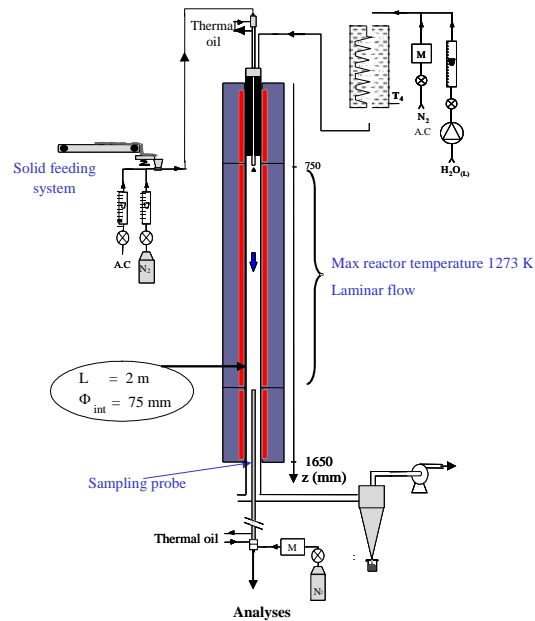
Figure 1: Scheme of the Entrained Flow Reactor

A sampling tube cooled by thermal oil is placed from bottom at different heights inside the reactor and aspirates a representative part of the gases and solids for analyses. Thus the residence time inside the reaction zone is controlled. Its calculation for solid takes into account the particle slip velocity, which is comparable with the gas velocity for 0.4 mm particles and about ten times higher than the gas velocity for 1.1 mm particles.

The sampled part is sent to a decantation pot in which the solid is collected, then the gas mixture is sent to a filter that retains fine particles and most remaining tars. All the sampling line is heated up to a condenser which is cooled by a glycol-water mixture. This condenser is used to collect most of the water contained in the gas. At the outlet of the condenser, the gas is analyzed by:

- a Fourier Transformed Infra Red (FTIR) spectrometer (CO, CO_2, CH_4, C_2H_4, C_2H_2, C_2H_6)
- a paramagnetic analyser (O_2)
- two Flame Ionisation Detectors (FID) (CH_4, total hydrocarbons)
- a Katharometer (H_2)
- an hygrometric mirror (H_2O contained in gas at ambient temperature).

The mass of solid residue is calculated through the ash tracer method [1].

The main operating conditions of the experiments are summarized in table II.

Table II: List of experiments

Particle size	Steam in feed gas(vol%)	Temperature (K)	Solid residence time (s)
0.4 mm	0	1073; 1173; 1273	0.35; 0.45; 0.55; 0.75;
	0;20	1073; 1223	1.00
1.1 mm	0	1073; 1223	0.30; 0.40; 0.45

2.3 Mass and elemental balances

Mass balances are made over the collected gas and the solid recovered in the collecting pot; tars trapped on the filter and hydrocarbons in the water condenser are not considered. The balances are satisfied within about 10 wt% uncertainty for each experiment.

3 RESULTS AND DISCUSSION

Within the range of study, the most influential parameter on the results was the particle size. That is the reason why the results are separated into two sub-sections, each one being devoted to one particle size.

3.1 0.4 mm particles

3.1.1 ESEM observations on the solid residue

In figures 2 and 3 ESEM pictures are shown of the initial biomass and of solid residue obtained at 1073 K under N_2 atmosphere and a solid residence time of 1.0 s.
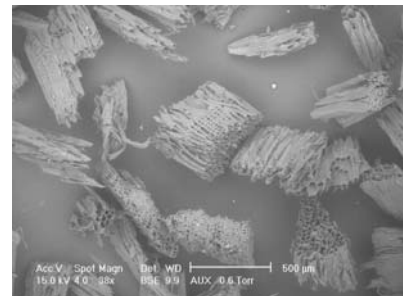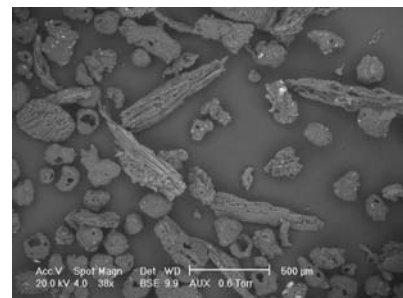

Figure 2: Initial wood (0.4 mm particles)

Figure 3: Residue obtained after an experiment (100 % N_2; 1073 K; solid residence time: 1.0 s)

The solid residue seems to be made up of two different kinds of particles:
- Particles that have kept the fibrous structure of wood and the aspect of thick slabs;
- Particles that have completely lost the initial wood structure and that look like exploded spherical shells of reduced size (about 0.1 mm), with small pores on their walls.

The outer surface of these two kinds of particles is mainly made of carbon, with a very low level of oxygen. This proves that even the fibrous particles are not wood anymore.

3.1.2 Gas-solid distribution

As can be seen in figure 4, more than 75 wt % of the

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initial biomass is converted into wet gas and the amount of solid residue is low, of about 7 to 10 wt %, whatever the operating conditions are (1073 K<T<1273 K ; solid residence time between 0.3 and 1.0 s). This proves that the decomposition of 0.4 mm particles is near completion after 0.3 s for temperatures greater than 1073 K.
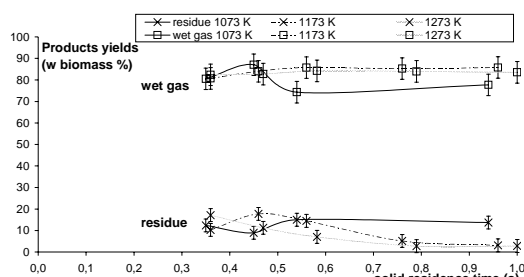

Figure 4: Yields of wet gas and residue versus solid residence time in the temperature range 1073 K - 1273 K

3.1.3 Mean gas yields

The standard deviations on the gas yields have been calculated from the whole set of experiments performed under N_2 feed gas. As can be seen in table III, they are quite small on most major gases, namely CO, CO_2 and CH_4. They are a little higher on H_2, C_2 species and H_2O. Globally speaking, the gas composition is not very sensitive to the tested parameters (1073<T<1273 K; residence time: 0.3-1.0 s).

Table III: Mean gas yields and standard deviations (between brackets) for experiments under N_2 on 0.4 mm particles

	mol wet gas%	w dry biomass%
H_2	20.9 (6.5)	1.8 (0.7)
CO	44.4 (3.8)	53.4 (2.4)
CO_2	3.0 (0.5)	5.7 (1.0)
CH_4	7.9 (1.5)	5.4 (0.8)
C_2H_4	2.3 (1.2)	2.7 (1.3)
C_2H_2	2.5 (0.6)	2.8 (0.9)
C_2H_6	0.0 (0.0)	0.0 (0.0)
H_2O	19.0 (4.7)	14.6 (3.8)

The figures 5, 6 and 7 give the mean distribution in the products of the elements C, H and O initially contained in biomass. It can be seen that about 50 % of the initial carbon is converted into CO. Less than 5 % is found in CO_2, leading to a molar ratio CO_2 to CO below 0.1. H_2 and H_2O are the other main gases, each one containing about 25 % of the hydrogen initially contained in biomass. About 20 % of the hydrogen is not recovered and this may be partly attributed to light hydrocarbons between C_3 and C_6 and tars. The remaining 30 % are converted into light hydrocarbons (CH_4, C_2H_2, C_2H_4). Among these three species, CH_4 is the major one. Nevertheless, the C_2 species are not negligible with about 10 % of the initial carbon and hydrogen.
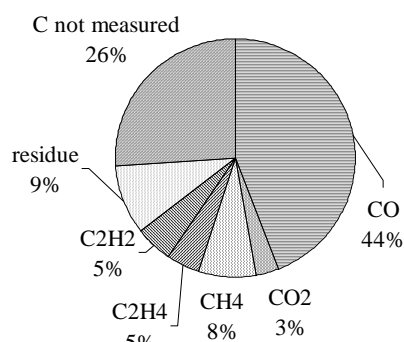

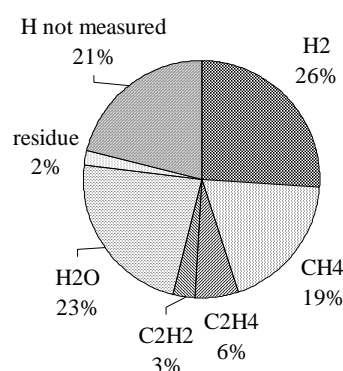Figure 5: Distribution of the element C in the products (0.4 mm particles; T=1173 K; solid residence time=1.0 s; 100 % N_2)

Figure 6: Distribution of the element H in the products (0.4 mm particles; T=1173 K; solid residence time=1.0 s; 100 % N_2)
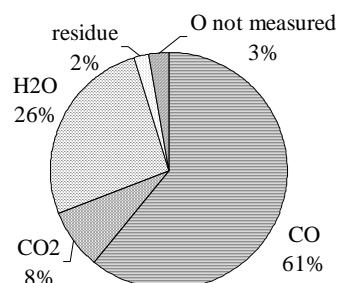

Figure 7: Distribution of the element H in the products (0.4 mm particles; T=1173 K; solid residence time=1.0 s; 100 % N_2)

3.1.4 Gas yields versus temperature and residence time

Gas yields are plotted for different temperatures versus solid residence time in the range [1073–1273 K] in Figures 6, 7 and 8.
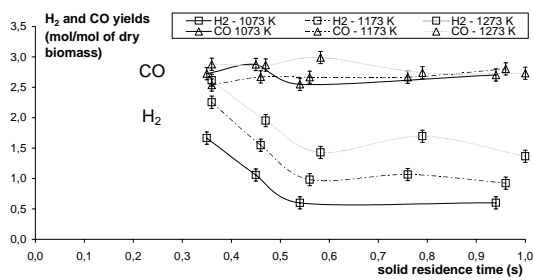
Figure 6: H_2 and CO yields versus solid residence time in the temperature range 1073 K - 1273 K
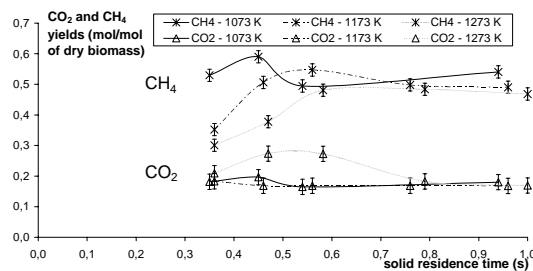

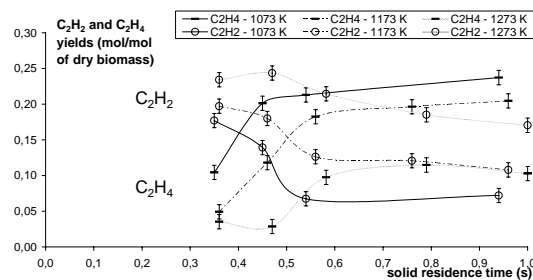Figure 7: CO_2 and CH_4 yields versus solid residence time in the temperature range 1073 K - 1273 K

Figure 8: C_2H_2 and C_2H_4 yields versus solid residence time in the temperature range 1073 K - 1273 K

To explain the trends observed on the graphs, two assumptions are made. Firstly, the solid decomposition is finished before 0.35 s. Secondly, the gas-solid reactions are too slow to occur inside the reactor under the conditions of the study. Therefore, the evolutions of the gas phase composition may only be attributed to homogeneous reactions (including the reactions with tars).

If only the five main species (H_2, CO, CO_2, CH_4, H_2O) are considered, the gas phase composition is governed by two independent reactions: the steam reforming of CH_4 and the water-gas shift [3]. For these two reactions, the equilibrium constant can be compared with the reaction constant calculated with the partial pressures of the different gases from the experiments. Results obtained at different temperatures are shown in Table IV.

As expected according to [3], the steam reforming of CH_4 is far from equilibrium within this range of temperatures.
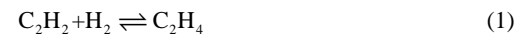
The water-gas shift does not attain equilibrium under the conditions of the experiments, even if the ratio between the reaction constant and the equilibrium constant is closer to 1 at 1273 K. These results are in accordance with those of Zanzi [4], obtained in a free-fall reactor under comparable conditions to ours. Thus, for modelling

purpose, this implies that the water-gas shift has to be considered as kinetically limited within the range of temperatures 1073-1273 K when the gas residence time is shorter than 10 s.

Table IV: Comparison between experimental reaction constant and equilibrium constant of water-gas shift and steam reforming of CH_4

Temperature	K	1073	1273
Gas residence time	s	3.2	3.2
Water-gas shift			
$K_{shift\ exp}$	-	0.05	0.19
$K_{shift\ éq}$	-	1.04	0.57
$K_{shift\ exp}/ K_{shift\ éq}$	-	0.05	0.32
Steam reforming of CH_4			
$K_{ref\ CH4\ éq}$	-	0.06	0.7
$K_{ref\ CH4\ exp}$	-	170	9280
$K_{ref\ CH4\ exp}/K_{ref\ CH4\ eq}$	-	3.4×10^{-4}	7.3×10^{-5}

The H_2 yield is clearly favoured from 1073 K up to 1273 K, with a total increase of about 1 mol/mol of dry biomass. Between 0.3 and 0.55 s, there is a strong decrease of the amount of H_2, with a decrease of about 1 mol/mol of dry biomass, that is more than 50% of the total yield. H_2 and C_2 species clearly seem to be correlated: H_2 and C_2H_2 follow similar trends, whereas C_2H_4 evolves symmetrically to them. Based on these observations, the assumption can be made that the following reaction of hydrogenation occurs inside the reactor:

$$C_2H_2 + H_2 \rightleftharpoons C_2H_4 \qquad (1)$$

Since the reverse reaction is thermodynamically favoured when temperature increases, this could explain why C_2H_4 tends to decrease with temperature in favour of C_2H_2. However, quantitatively speaking, this reaction can only explain about 10 % of the decrease observed on H_2 with residence time. Therefore it may be suggested that other reactions also occur that involve heavier hydrocarbons and H_2.

3.1.5   Gas yields in the presence of steam

Dry gas yields are plotted in Figure 9 for experiments performed under 100 % N_2 and a mixture of 80 vol% N_2+20 vol% H_2O feed gas.
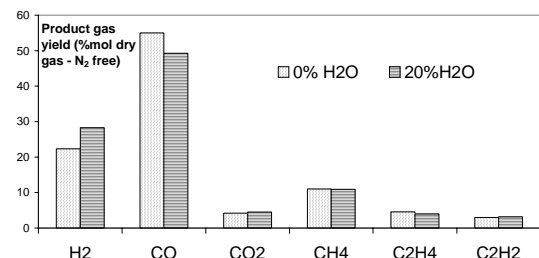

Figure 9: Influence of the presence of steam in the atmosphere (T=1223 K; ts=0,55 s)

At both temperatures, the presence of steam clearly influences the yields of H_2 and CO. The amounts of the other gases do not seem to be significantly affected, except C_2H_4, whose yield slightly decreases in the presence of steam at 1223 K. Quantitatively, the increase of H_2 yield, of about 6 mol %, seems to be well-balanced

by the decrease of CO. This can be explained by the reaction of water-gas shift. However, this would imply a correlative increase in CO_2 yield, which is not observed. To explain this discrepancy we need to invoke a heterogeneous reaction with the residue, namely:

$$C + CO_2 \rightleftharpoons 2CO \qquad (2)$$

But it is well-known that under the studied conditions of temperature, this reaction is strongly kinetically limited [5]. We have thus no satisfactory explanation for the contradictory behaviours of H_2, CO and CO_2.

The absence of influence of steam on CH_4 confirms that the steam reforming of CH_4 is kinetically blocked under our conditions. The same assessment can be made about the steam reforming of C_2H_2 at 1073 K and 1223 K, and of C_2H_4 at 1073 K. However, at 1223 K, the yield of C_2H_4 significantly decreases, which could be the evidence for steam reforming. The steam cracking of heavier hydrocarbons may also occur, since these products are less stable than CH_4 or C_2 species. This could explain the increase of H_2 yield, but these reactions would also produce CO, which is contradictory with its decrease.

3.2 1.1 mm particles

3.2.1 Preliminary remark

The experiments on 1.1 mm particles are limited to a narrow range of solid residence times, between 0.25 s and 0.45 s. This is due to the high slip velocity of the 1.1 mm particles.

3.2.2 Solid consumption regime

Initial wood and an example of residue obtained after pyrolysis are shown in Figures 15 and 16.
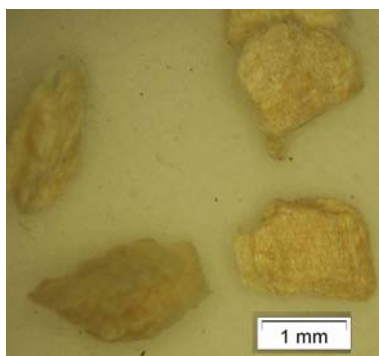

Figure 15: Initial wood (1.1 mm)

Figure 16: Wood particle after pyrolysis (T=1073 K; solid residence time = 0.45 s)

The particle of residue is darkened only on its edge on a thickness of about 0.1 mm after 0.45 at 1073 K. Its centre still looks like wood. There seems to be a front of reaction moving towards the particle centre. This suggests limitations by internal heat transfers. This seems to be in agreement with the characteristic time of internal conduction calculated for particles of 1.1 mm, that is about 0.1-1.0 s [3].

3.2.3 Results concerning gases

Gas yields are given in Table V for different temperatures (1073 K; 1223 K) and solid residence times.

Table V: Gas yields for pyrolysis of 1.1 mm particles

T	K	1073	1073	1223	1223
Solid residence time	s	0.3	0.45	0.3	0.45
Wet gas	w%	14	20	19	35
Dry gas	w%	2	8	9	25
H_2		Nd^a	0.04	0.1	0.35
CO		0.1	0.3	0.4	1.0
CO_2	mol/mol dry biomass	Nd	0.01	0.02	0.08
CH_4		0.01	0.05	0.06	0.17
C_2H_4		0.01	0.03	0.03	0.09
C_2H_2		0.004	0.015	0.03	0.07
H_2O		1.1	1.1	0.8	0.8

[a] Not detected

Under the conditions of study (1073<T<1223 K; solid residence time: 0.25-0.45 s), the maximum total gas yield is of 35 wt % of the initial biomass, which is about half of the conversion observed for 0.4 mm particles. The dry gas yield is clearly favoured by the increase of temperature and residence time. This shows that the reaction is still in progress after 0.45 s under these conditions of temperature, which is in agreement with the observations made on solid residues.

Trends are similar when each component of the dry gas is considered separately. On the contrary, the yield of steam does not seem to depend on residence time and its amount slightly decreases with temperature, from 1.1 mol/mol dry biomass to 0.8 mol/mol dry biomass. These values are comparable with the amount of water contained in biomass as moisture, which is of about 0.75 mol/mol dry biomass. This would mean that the measured steam mainly comes from drying, which is over after 0.30 s. Drying and pyrolysis would therefore occur almost sequentially under these conditions of temperature (1073 K;1273 K) for particles of 1.1 mm.

4 CONCLUSIONS

Flash pyrolysis experiments are done under N_2 and a mixture of N_2 and steam using a mixture of softwoods in an Entrained Flow Reactor between 1073 K and 1273 K. The results are very dependent on the particle size in the range under study (0.4 mm and 1.1 mm).

Under these temperatures (1073 - 1273 K), the decomposition of the 0.4 mm particles seems to be finished after a solid residence time smaller than 0.5 s, with more than 75 wt % of the initial mass of biomass converted into gas. The decomposition of the 1.1 mm

particles does not reach completion at 0.5 s. and seems clearly limited by heat transfers. In this last case, drying is apparently finished at 0.3 s.

It has also been shown that the main gas phase species produced during pyrolysis do not much evolve under the studied range of gas residence time that is of a few seconds. Only H_2 seems to be notably influenced, probably due to reactions with light hydrocarbons such as C_2 and with tars, not measured here. The other possible reactions seem to be kinetically blocked, notably the steam reforming of CH_4 and the steam cracking of C_2. The water-gas shift reactions is kinetically controlled and is close to equilibrium at the highest temperature and gas residence time investigated (1273 K, 3.5 s); it is probably favoured by the presence of an excess of steam.

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