

# Hydrogen Enrichment in the Catalyzed Gasification of Sawdust

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**Abstract**— The influence of the nickel-based catalyst on the content of hydrogen gas produced by the gasification of sawdust and its effect on organic impurities (tars) at the pilot plant scale is studied. The effect of the reaction temperature of the catalytic stage in the range 800-900 °C and the use of steam as an oxidizer is analyzed. For this temperature range, the content of hydrogen in the gas mixture increases with the increase in temperature as with the increase in the biomass vapor ratio.

**Keywords**— Gasification, Hydrogen, Catalyst, Sawdust.

## I. INTRODUCTION

In biomass gasification it is appropriate to study how to raise the level of hydrogen yield in the product gas mixture (CO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O). The thermal conversion processes (pyrolysis-gasification) involve the formation of particulates and tars, a complex mixture of condensable aromatic and polyaromatic hydrocarbons, the way to prevent the formation of tars during the gasification process presents significant light and dark [1]. The presence of tars causes problems linked to condensation and clogging of process equipment, formation of tar sprays and polymerization of more complex structures [2,3]. The yield and tar composition depend on the reaction temperature, the type of reactor as the raw material [4]. The various alternatives for tar removal can be summarized in two groups: a) in-situ reduction (or principal) of tar which prevents tar formation; b) reduction after gasification (or secondary), reduction that eliminates the product tar gas already produced. To increase the production of hydrogen gas, the use of sorbents and catalysts is recommended, linked to the effect on the decomposition of tar [5,6]. The nickel catalyst participates mainly by accelerating the hydrocarbon reforming reactions with water vapor, reforming hydrocarbons with (CO<sub>2</sub> - dry reforming) and in the WGS (reversible gas water) in the direction of steam formation of water and carbon monoxide.

## II. MATERIALS & METHODS

The equipment used for the gasification experiments is constituted by a gasifier reactor, a cyclone separator of coarse and incandescent particulates and a second reactor as catalyst reactor, shown in Fig. 1. Both reactors resistively heated with insulation in ceramic fiber.

The feeding of the biomass (sawdust pellets) is carried out in the upper part of the gasifier reactor in a fluidized regime, manually using a series valve device. The product gas is conducted by the outlet pipe to the catalytic reactor, thermally insulated pipe to avoid the formation of condensates, with a cyclone solid separator prior to entering the catalytic reactor. The samples taken, indicated in Fig. 1, are made by online

method and their collection in Tedlar bags for their chromatographic analysis.

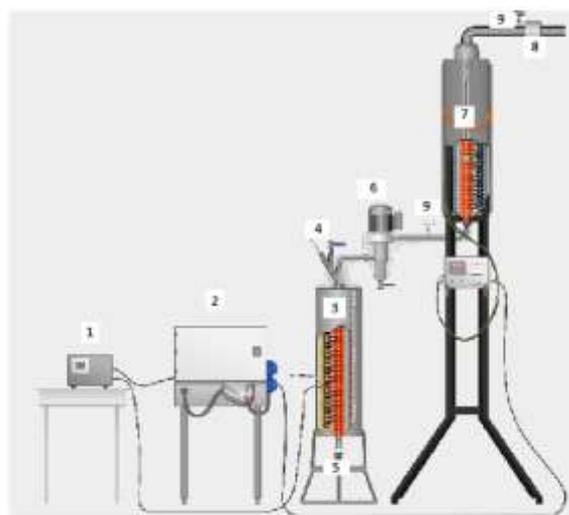


Fig. 1. Outline set equipment

1. Gasifier-2. Controller board -3. Gasifier reactor -4. Biomass feeder-5. Combustant feed-6. Cyclone-7. Catalysis reactor-8. Extractor-9. Samples

The experiments were carried out using an air and steam oxidizing agent, by means of an air impulsion device at the inlet of the gasification reactor as a steam generator at the same point. For the analysis of the gasification products of the experiments carried out, a SRI GC 310C gas chromatograph, with thermal conductivity detector and packed column RESTEK Shin Carbon ST 80/100 ID is used. For the analysis of the tars, a Varian liquid chromatograph, model ProStar 210 with a UV / Vis detector model ProStar 320 was used, with Rheodyne 7725i manual injector with an injection loop of 20 ul.

The biomass raw material consists of sawdust pellets provided by a timber company in the province of Misiones, with specifications according to table 1.

TABLE 1. Pellets properties

$\phi$	L	M	$\rho$ (kg/m <sup>3</sup> )	P	ash	H
6.2	21 – 25	0.6 0–0.70	1330	19.23	< 4	10-15
6.2	11.3 – 15	0.37 – 0.50				
6.2	5 – 8	0.30 – 0.40				

$\phi$ : pellet diameter x10<sup>-3</sup> (m); L: pellet length x10<sup>-3</sup> (m); M: pellet weight x10<sup>-3</sup> (kg);  $\rho$ : density (kg/m<sup>3</sup>); P: heat value (Mj/kg); Ash: %; H: moisture (%)

The solid auxiliary material is siliceous, oven-dried sand, which was subjected to size classification using set of screens

20, 35, 40, and 45. The sand is within the fluidizable group B of the classification Geldart [7].

The catalyst, in the form of pellet cylinders of 0.002 m x 0.004 m, has the following characteristics: 9.9% Ni on  $\gamma$  alumina, prepared in the laboratory of INCAPE-FIQ-UNL (Santa Fe-Argentina).

### III. RESULTS & DISCUSSIONS

The tests to guarantee the adequate hydrodynamic behavior in fixed bed regime, led to a maximum load value of solid catalyst of 0.010 kg, for given operating levels.

Biomass flow rate: up to 0.4 kg biomass / h. Sandy bed: up to 0.002 m high. Gasifying agent speed (air-steam): 0.06-0.12 m/s, steam feed 0.1-0.4 kg/h. Reactor gas temperature: 850 °C. Catalytic reactor temperature: 800-900 °C. Catalytic bed solid: up to 0.010 kg.

For gasifier temperature of 850 °C, adopted as the most appropriate for the gasification stage and catalytic reactor temperatures of 800-825-850-875-900 °C, the experimental values of the concentrations in Table 2, expressed in percentages, are reported.

The percentage of hydrogen in the product gas increases through its passage through the catalytic reactor, this increase is directly related to the temperature of the catalytic process, according to the experimental values of Table 3, expressed in percentages.

TABLE 2. Experimental values with catalytic action

Products	800 °C	825 °C	850 °C	875 °C	900 °C
H <sub>2</sub>	42.17	40.75	43.04	45.18	46.00
CO	52.03	49.7	50.5	50.8	50.10
CO <sub>2</sub>	0.43	0.6	0.61	0.62	0.46
CH <sub>4</sub>	1.08	1.2	1.00	1.00	1.01
O <sub>2</sub>	3.0	4.23	4.70	2.3	2.3

TABLE 3. Effect of catalysis on concentrations

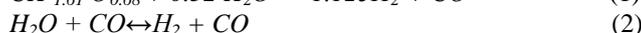
Gas (%)	Gasificator effect of 800-850 °C	Efecto cataliyst (T=900 °C) (respec to T gasif=850 °C)
H <sub>2</sub>	32.8-35.6=2.8% increase	46.00%; increase 10.4%
CO	41.8-56.2=14.4% increase	50.1% decrease 6.1%
CO <sub>2</sub>	2.0-2.2=0.2% decrease	0.46%; decrease 1.74%
O <sub>2</sub>	18.35-4.68=13.5% decrease	2.3%; decrease 2.38%
CH <sub>4</sub>	2.1-1.1=1.0 % decrease	1.01%; decrease 0.09%

T: temperature

The influence of the vapor on the content of hydrogen gas in the gas mixture (with and without catalytic stage) is studied and the kinetic constant of the process is calculated, Fig. 2

Studied temperature level: 850 °C for gasificator reactor and catalytic reactor, biomass feed: 0.4 kg/h, dry base moisture: 15%, v/b ratios (steam/biomass): 0.4-0.46-0.7-0.9.

It is defined RE: stoichiometric yield of hydrogen, obtainable considering the reactions (1) and (2) and its stoichiometry



The yield in hydrogen Yh, using various ratios of steam to biomass, v/b (kg vapor/kg biomass), fH (mol hydrogen / biomass/stoichiometric hydrogen yield, Yh / RE), according to:  $d fH/d (v (b)) = d (fH) / d (v (b)) = kH (1-fH)$  (3)

The values to obtain the linear regression are shown in table 4.

TABLE 4. Table of values for constant kinetic calculation at 850 °C gasifier reactor and catalytic reactor at 850 °C

H <sub>2</sub> (%)	Yh(molH <sub>2</sub> /kg biomass)	fH=Yh/RE	-ln(1-fH)	v/b
46	12.32	0.142	0.153	0.4
48.5	12.99	0.149	0.161	0.46
50	13.39	0.154	0.167	0.7
52.2	13.98	0.161	0.175	0.9

H<sub>2</sub>: chromatographic value(%)

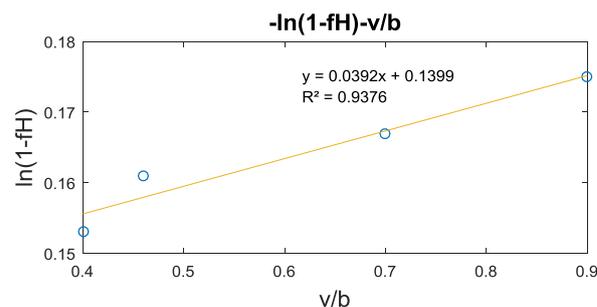


Fig. 2. Constant kinetic calculation (850-850 °C)

A value of kH = 0.0392 is obtained. The study is extended for other temperatures of the catalytic reactor, namely 825 °C and 875 °C, as the one corresponding to the gasification process without catalytic stage, results that are shown in table 5.

TABLE 5. Summary table

Gasificator reactor T °C	Catalytic reactor T °C	kH
850	---	0.0128
850	825	0.016
850	850	0.0392
850	875	0.0188

Increased hydrogen content is manifested with the increase of the steam / biomass ratio and with the increase of the temperature level.

#### Treatment of tars and kinetics

Studies on the decrease-elimination of tar can be considered taking model compounds. In the present work, benzene and toluene were used as tars, since they represent relatively stable and representative aromatic compounds in gasification processes at elevated temperatures [8].

The residence time factor is  $\Theta$  (kg / (m<sup>3</sup> / h), Xalq (tar conversion), catalyst weight (0.075- 0.010kg), product gas flow at the catalyst reactor outlet (m<sup>3</sup>/h), obtainable experimentally.

Is calculated:

$$kap = -\ln (1-Xalq) / \Theta \quad (4)$$

with kap, apparent kinetic constant, under the assumption of a first-order reaction; with these kap values, ln kap vs (1 / T) is plotted in K, generating the linear regression, allowing finding the activation energy in terms of kap and T, responding to the Arrhenius model.

Monitoring benzene in biomass tar: catalyst weight 0.010 kg, average exit flow: 0.212 m<sup>3</sup>/h.

Temperatures to be processed:  $T$  gasifier reactor 850 °C,  $T$  catalytic reactor: 850-875-900 °C (table 6).

TABLE 6. Table of values for constant kinetic calculation of tar decrease (benzene)

$T_{gasif}$	$T_{cat}$ °C(K)	$X_{benzene}$ %	$\theta$	$Ln\ kap$
850	875(1148)	0.4106-0.0485=88.2	0.045	3.86
850	900(1173)	0.4205-0.0487=88.4	0.045	3.87
850	850(1123)	0.411-0.0495=87.9	0.045	3.85

$T_{gasif}$ : gasifier reactor temperature  
 $T_{cat}$ : catalytic reactor temperature

These values as pairs  $ln\ kap-1/T$  (K), based on the Arrhenius equation, are plotted to find the  $E_a$  (activation energy) and  $k_0$  (pre-exponential factor), Fig. 3.

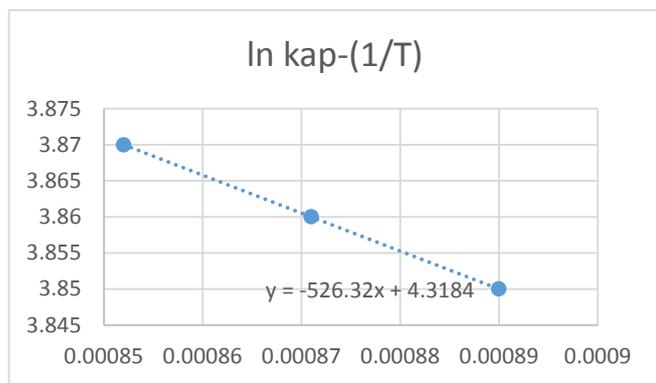


Fig. 3.  $kap-1/T$  (benzene)

$E_a = 4.375\text{ kJ/mol}$ ;  $k_0 = 75.06\text{ m}^3/\text{kg h}$

The toluene monitoring in biomass tars is reproduced in table 7

TABLE 7. Table of values for constant kinetic calculation of pitch decrease (toluene)

$T_{gasif}$	$T_{cat}$ °C(K)	$X_{toluene}$ %	$\theta$	$kap$
850	850(1123)	0.4589-0.3639=20.70	0.045	4.65
850	875(1148)	0.468-0.376=19.65	0.045	4.86
850	900(1173)	0.471-0.382=18.89	0.045	5.15

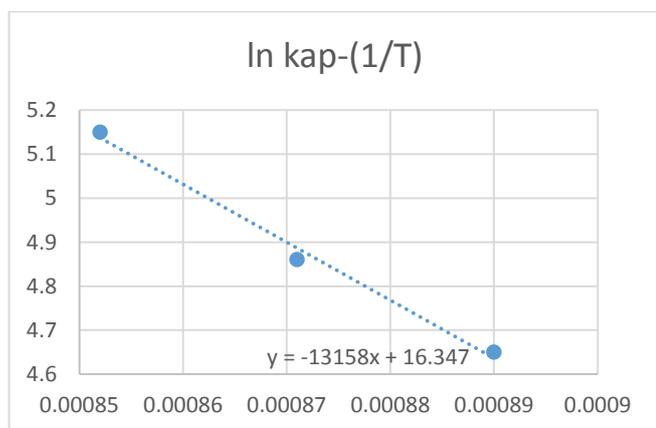


Fig. 3.  $kap-1/T$  (toluene)

$E_a = 109.342\text{ KJ/mol}$ ;  $k_0 = 1,25 \times 10^7\text{ m}^3/\text{kg h}$

According to the simple model proposed, the rate constant for the elimination of tars (benzene and toluene) increases

with temperature, as an outstanding element for the choice of operating variables.

#### IV. CONCLUSIONS

The effect of the catalysis on the content of hydrogen gas and its concentration after the gasification registers a clear increase in the values obtained experimentally, using air as an oxidizing agent.

In this improvement in the concentrations of the hydrogen species, the influence of the temperature, at higher temperature of the catalytic reactor, higher content of hydrogen gas, the temperature limits set by the limitations of the exposure temperature of the catalyst support used together are marked. to the possibilities of plant equipment.

The use of steam as a gasifying agent, for steam / biomass ratios between 0.4-0.9, exerts a positive effect on the increase of hydrogen gas content, in the case of the gasification stage of 2% regarding the use of air, for the same operating temperature (850 °C).

The catalytic action maintains and reinforces the positive action on the concentration of hydrogen gas, for the same steam / biomass ratios, registering increases of 3-6%, for temperatures of 800 °C, 825 °C, 850 °C, and 875 °C, on the values obtained for the catalysis with the use of air as a gasifying agent.

The effect of catalysis on the decrease of the tar content [9], taking benzene and toluene as representative compounds of the tar in the biomass gasification, shows a significant degree of conversion of compounds, in the case of benzene of the order of 90% and 20% % in the case of toluene, with the values of the kinetic constant (for supposition of reaction rate of order one) increasing with the increase of temperature (850, 875, and 900 °C), indicating the efficiency of the use of the nickel-based catalyst for the action of decrease and / or elimination of tars.

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