

下吸式气化炉木屑高温蒸汽气化制取富H₂实验*

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摘要: 设计了生物质高温蒸汽气化实验平台,主反应器为高温蒸汽发生系统和带有喉口的下吸式气化炉。利用该实验平台对木屑进行高温蒸汽气化研究,气化过程通入的蒸汽温度控制在 600 ~ 1 000℃。实验结果表明:高温蒸汽既是气化过程的气化剂又是部分热载体,能有效提高气化效率,并维持炉内温度场的稳定。实验条件下,气化气可燃组分体积分数达到 77% 以上,当蒸汽温度为(948 ± 4)℃时,气化气中 H₂ 体积分数达到(51.83 ± 0.12)%,气体热值为 9.81 MJ/m³, H₂/CO 组分比达到 2.17,气化气可持续稳定燃烧,气化性能较为理想。

关键词: 木屑 高温蒸汽气化 下吸式气化炉 富氢气体

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Performance of Downdraft Gasifier for Hydrogen-rich Gas by High Temperature Steam Gasification of Biomass

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Abstract: In recent years, high temperature steam gasification (HTSG) is a new gasification technology which utilizes super-heated, high temperature steam as gasifying agent as well as partial heat carrier. A HTSG experimental platform for generating hydrogen-rich gas from biomass was proposed. The experimental platform included a high temperature steam generating system, a downdraft gasifier, a gas purification system, a sample gas collection system and an automatic control system. The gasification performance of the downdraft gasifier was evaluated by using pine wood shavings which considered the effects of reaction temperature. The steam temperature was controlled from 600℃ to 1 000℃ during experiment. The results showed that combustible gas composition over volume fraction of 77% was obtained in these experiments. The volume fraction of H₂ increased and CO and CH₄ decreased as the reaction temperature increased. When steam temperature was (948 ± 4)℃, the volume fraction of H₂ reached (51.83 ± 0.12)%, the lower heating value of produced gas was 9.81 MJ/m³, composition ratio of H₂/CO reached 2.17 and the gas produced by high temperature steam gasification can be stable to burn, thus the gasification performance was regarded as relatively perfect. High temperature steam gasification is an effective way by using biomass such as pine wood shavings for making hydrogen rich gas, and it has the huge development potential and application space. The results could provide guidance for gasifier and engineering design of the biomass gasification.

Key words: Biomass High temperature steam gasification Downdraft gasifier Hydrogen-rich gas

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引言

化石燃料引发的温室效应和环境污染日趋严重,促使清洁能源的开发和利用成为全世界的研究热点。生物质能是重要的可再生能源,气化工艺能够将生物质转化为使用方便的清洁气体燃料或合成气原料气。氢作为一种理想的洁净能源载体,被誉为 21 世纪的绿色能源和人类的未来能源^[1]。生物质蒸汽气化技术具有氢气含量高、不含氮气的优势,但传统蒸汽气化技术采用的蒸汽温度多为 100 ~ 150℃^[2],由于气化过程需吸收大量热量,该技术存在气化效率低,焦油含量高,燃料利用范围小等问题。为提高气化气的质量,许多学者^[2-9]将蒸汽温度提高到 600℃ 以上,对不同生物质进行了高温蒸汽气化 (High temperature steam gasification, HTSG) 技术的研究。结果表明高温蒸汽气化所得气化气中 H₂ 含量可达 40% ~ 60%,较传统蒸汽气化所得 H₂ 含量 (约为 20% ~ 26%)^[10] 有了较大幅度的提高。

气化技术按炉型可分为固定床、流化床和气流床等类型。下吸式气化炉属于固定床的一种,具有结构简单、工作稳定、焦油含量低等特点,在农村集中供气及小型生物质发电技术中得到了广泛的应用^[11]。本文自行设计了生物质高温蒸汽气化实验

平台,主反应器为高温蒸汽发生系统和带有喉口的下吸式气化炉。利用该平台对木屑进行蒸汽气化实验研究,通过实验分析气化炉内蒸汽温度与生成气化气中氢气含量、气化气成分及燃气热值的变化关系,得到该气化炉的气化性能,同时进一步分析生物质高温蒸汽气化的热力学机理。

1 高温蒸汽气化实验

1.1 实验装置

生物质高温蒸汽气化实验平台示意图如图 1 所示,包括:高温蒸汽发生系统(A)、下吸式气化炉(B)、气体净化系统(C)、样气采集系统(D)和控制系统(E)等 5 部分。本实验平台^[12] 设计上有 2 个特点:①采用高温蒸汽进行气化,蒸汽温度控制在 600 ~ 1 000℃,由高温蒸汽发生系统得到。蒸汽由电热蒸汽发生器产生,蒸汽流量(0.89 ± 0.02) kg/h,蒸汽压力为(0.300 ± 0.004) MPa。产生的蒸汽如图 1 所示由电加热装置加热后送入气化炉内。②气化炉采用中间带有喉口(截面直径 60 mm)的双锥形结构,上锥段(截面直径 180 mm)收缩符合炉内物料热解后体积缩小的特征,下锥段(截面直径 120 mm)渐扩便于物料的下降,但其直径小于上锥段,主要考虑了生物质物料含有大量挥发分,固定碳含量较少

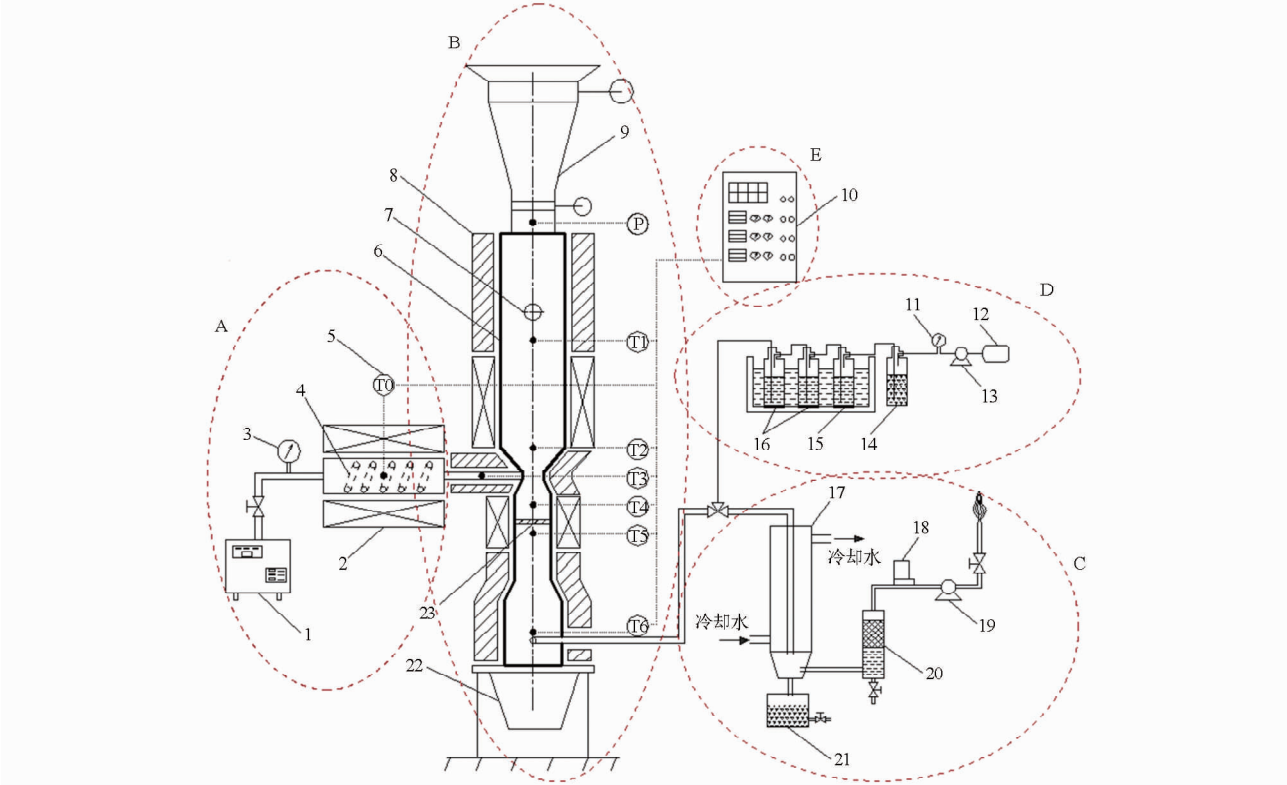


图 1 生物质高温蒸汽气化实验平台示意图

Fig.1 Schematic diagram of experimental platform for high temperature steam gasification of biomass

1. 蒸汽发生器 2. 电加热装置 3. 流量计 4. 盘管 5. 温度测点 6. 炉胆 7. 窥孔 8. 保温砖 9. 料斗 10. 控制柜 11. 流量计 12. 集气袋
13. 真空泵 14. 无水氯化钙 15. 异丙醇 16. 水 17. 冷凝器 18. 煤气表 19. 真空泵 20. 净化装置 21. 焦油收集装置 22. 灰斗 23. 炉排

(相比煤而言)。该结构有利于气化物料在炉内形成“整体流”,有效减轻架桥结拱倾向^[13]。此外,由于采用高温蒸汽气化,气化炉料斗设计为双翻板式以实现密封加料。图 2 为实验平台照片。



图 2 实验平台照片

Fig. 2 Photograph of experimental platform

1.2 温度及压力测量

如图 1 所示,炉体由上至下共布置 6 根热电偶,定义如下:T1 ~ T6 分别对应测量气化炉内的干燥区、热解区、蒸汽、还原区 1、还原区 2 和气化气出口的温度。每 10 min 记录 1 次热电偶的温度值。炉内压力监测点布置在气化炉进料口下部。每 10 min 记录 1 次压力。

1.3 实验物料及气体成分检测

实验生物质原料采自包头市某木材加工厂生产的松木木屑,如图 3 所示,经筛选后,粒径范围为 8 ~ 12 目。松木木屑元素分析和工业分析如表 1 所示,高位热值为 20.54 MJ/kg^[14]。



图 3 松木木屑样品

Fig.3 Pine wood shavings sample

表 1 松木木屑的元素分析和工业分析

Tab.1 Proximate and ultimate analysis of pine wood shavings

元素分析	元素组成	C	H	O	N	S
	元素质量	50.54 ± 0.03	7.08 ± 0.03	41.11 ± 0.03	0.15 ± 0.03	0.57 ± 0.03
工业分析	物质组成	挥发分	固定碳	灰分		
	物质质量	82.3 ± 0.8	17.1 ± 0.5	0.6 ± 0.2		
	分数/%	0.8	0.5	0.2		

气化气成分检测采用 Agilent 7890B 型气相色谱仪。

气化气热值计算式为^[15]

$$Q_L = 107.98\varphi_{H_2} + 126.36\varphi_{CO} + 358.18\varphi_{CH_4} + 629.09\varphi_{C_2H_m}$$

(1)

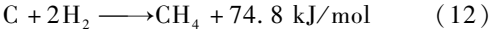
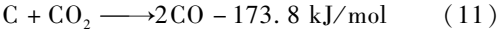
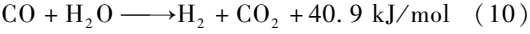
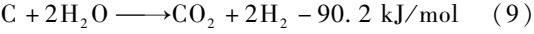
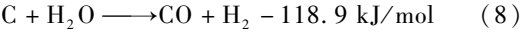
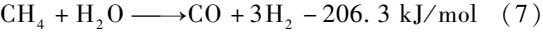
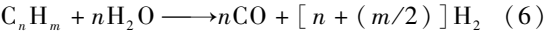
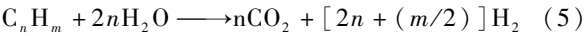
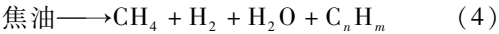
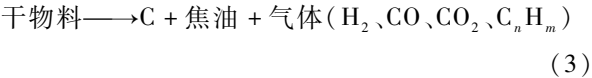
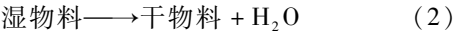
式中 Q_L ——标况下气体低位热值, kJ/m³

φ_{H_2} 、 φ_{CO} 、 φ_{CH_4} 、 $\varphi_{C_2H_m}$ ——产气中 H₂、CO、CH₄、C₂H_m 的体积分数, %

2 实验结果及分析

2.1 气化过程分析

高温蒸汽气化主要反应式^[16-18]为



大致可分为物料的干燥、热解和还原 3 个过程。首先,物料在气化炉内发生干燥过程,如反应式(2),温度在 100 ~ 150℃ 之间。当温度超过 200℃ 时^[19],物料开始发生热解,析出挥发分,温度越高,反应越剧烈。该过程的生成物成分较为复杂,主要为焦炭、焦油及 H₂、CO、CO₂、CH₄ 等不可凝气体,主要发生反应如式(3)。当高温蒸汽通入炉内后,主要发生焦油裂解反应如式(4)、蒸汽重整反应如式(5) ~ (7)、蒸汽还原反应如式(8)和式(9)、CO 变换反应如式(10)、CO₂ 还原反应如式(11)和甲烷化反应如式(12)。

由上可以看出,蒸汽气化主要为吸热反应,故本实验平台采用高温蒸汽作为气化剂和部分热载体,反应热量由高温蒸汽和外加热系统提供。这样有 2 个优点:一方面,高温蒸汽的加入较好地维持了炉内温度场的稳定,炉内温度分布更加均匀,避免了外加热炉内温度分布不均的缺点。另一方面,高温蒸汽在进入气化炉之前已经加热到 600℃ 以上的高温,可直接与炉内物料反应^[20],使反应时间大大缩短,提高了气化强度和气化效率。由图 4^[21]可以看出,温度越高,蒸汽的活性越高,能够给化学反应提供更多的热量,从而促进化学反应的发生。因此,以高温蒸汽作为气化剂可使蒸汽气化效率和氢气含量大幅提高。此外,高温蒸汽可与焦油等烃类化合物发生

重整反应,有效减少焦油的产生,使得气化反应中的焦油含量明显减少。文献[22]指出了蒸汽气化条件下的反应机理,如图5所示。虚线表示在高加热速率和高温条件下比较容易进行的路线,实线表示在中、高温加热速率和中温条件下较易进行的路线,点划线表示在低加热速度及低温条件下更易进行的路线。可以看出,在高加热速率和高温条件下可有效抑制焦油的生成。

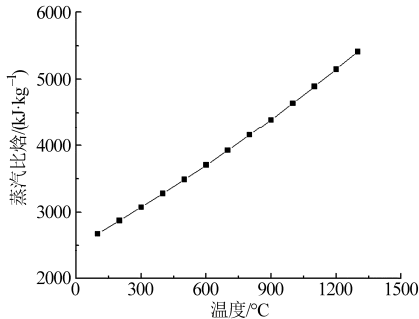


图4 蒸汽比焓随温度的变化关系(压力为0.1 MPa)
Fig.4 Steam enthalpy changes with temperature diagram under 0.1 MPa

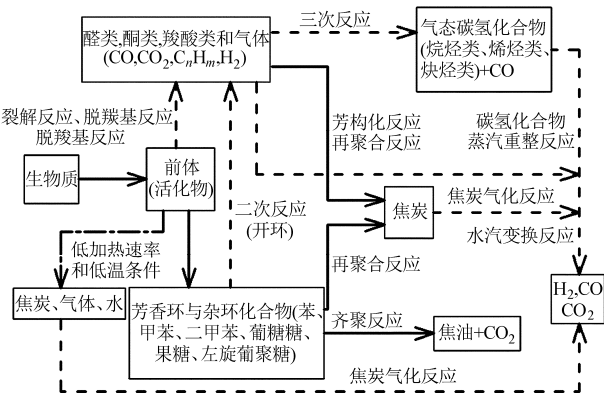


图5 生物质蒸汽气化反应机理
Fig.5 Reaction mechanism of biomass steam gasification

2.2 气化气成分分析

松木木屑高温蒸汽气化实验参数和气化气成分及热值如表2所示。实验中产生的气体可稳定持续燃烧,图6是反应温度为 $(948\pm4)^{\circ}\text{C}$ 时产生的气化气燃烧效果图。可以看出,火焰稳定,颜色为淡蓝色。

由表2可知,该气化实验可产生高品质的气体,主要组分为 H_2 和 CO ,占到了气化气总组分的70%左右,气化气可燃组分达到77%以上,气体热值为 $10\text{ MJ}/\text{m}^3$ 左右。研究发现,反应温度是影响气化效果的重要因素之一。当气化炉内通入蒸汽流量为 $0.89\text{ kg}/\text{h}$ 时,随着蒸汽温度的升高产气中 H_2 体积分数从 $(33.27\pm0.16)\%$ 升高到 $(51.83\pm0.12)\%$, CO 则从 $(34.97\pm0.03)\%$ 降低到 $(23.85\pm0.29)\%$, CO_2 的变化则不是很明显,该结果与文献[23]类似。主要因为此温度范围内蒸汽的还原反应(式(8))和 CO 变换反应(式(10))处于主导地

位,导致产气中 H_2 的含量增加, CO 的含量降低, H_2/CO 组分比则由0.95提高到2.17。此外,产气中 CH_4 和 C_2H_m 的含量随温度的升高均有所下降, CH_4 从 $(8.22\pm0.10)\%$ 降低到 $(2.32\pm0.07)\%$,这主要由于碳氢化合物与蒸汽发生重整反应(式(5)~(7)),且均为吸热反应,故温度升高有助于反应的进行。

表2 下吸式气化炉松木木屑高温蒸汽气化实验结果
Tab.2 Experimental results of pine wood shavings under high temperature steam gasification in a downdraft gasifier

参数	取样号		
	1	2	3
运行时间/min	10	30	60
蒸汽流量/ $(\text{kg}\cdot\text{h}^{-1})$	0.89 ± 0.02	0.89 ± 0.02	0.89 ± 0.02
蒸汽温度/ $^{\circ}\text{C}$	721 ± 4	832 ± 4	948 ± 4
H_2 体积分数/%	33.27 ± 0.16	48.39 ± 0.15	51.83 ± 0.12
CO 体积分数/%	34.97 ± 0.03	27.71 ± 0.02	23.85 ± 0.29
CH_4 体积分数/%	8.22 ± 0.10	2.91 ± 0.07	2.32 ± 0.07
C_2H_m 体积分数/%	0.91 ± 0.84	0.62 ± 0.37	0.58 ± 0.04
CO_2 体积分数/%	22.65 ± 0.62	20.38 ± 0.34	21.44 ± 0.18
H_2/CO 组分比	0.95	1.75	2.17
$\text{LHV}/(\text{MJ}\cdot\text{m}^{-3})$	11.53	10.16	9.81



图6 气化气燃烧效果图
Fig.6 Photograph of syngas burning

表3为生物质下吸式气化炉气化常用的2种气化技术(空气、富氧/蒸汽)^[24,14]与高温蒸汽对木屑气化产生的气化气组分的比较。可以看出:空气气化产气中含有大量的 N_2 ,稀释了燃气,气体热值也较低;富氧/蒸汽气化技术所产 H_2 和 CO 含量均有明显提高,但气化气中 CO_2 含量较高, H_2/CO 组分比较小,合成气利用受到限制。本文所采用的高温蒸汽气化制取的气化气中 H_2 含量和可燃气体成分最高,产气热值提高将近1倍。

3 结论

(1) 以木屑为原料的下吸式气化炉生物质高温

表3 生物质下吸式气化炉气体组分及热值

Tab.3 Gas composition and calorific value of biomass downdraft gasifiers

参数	气化技术		
	空气 ^[24]	富氧/蒸汽 ^[14]	高温蒸汽
喉口温度/℃	1 244	934	948 ± 4
H ₂ 体积分数/%	15.1	27.17	51.83 ± 0.12
CO体积分数/%	10.2	37.65	23.85 ± 0.29
CH ₄ 体积分数/%	0.9	4.78	2.32 ± 0.07
C ₂ H _m 体积分数/%	0.9	0.35	0.58 ± 0.04
CO ₂ 体积分数/%	14.7	28.89	21.44 ± 0.18
N ₂ 体积分数/%	57.4	—	—
H ₂ /CO 组分比	1.48	0.72	2.17
LHV/(MJ·m ⁻³)	11.53	9.75	9.81

蒸汽气化技术可制取富氢、中热值、清洁品质高的气

化气,是一种生物质气化的有效技术路线。实验条件下,气化气可燃组分达到77%以上,H₂体积分数最高达到(51.83 ± 0.12)%,热值为9.81 MJ/m³,气化气可持续稳定燃烧,气化性能较好。

(2) 生物质的高温蒸汽气化过程中蒸汽既是气化剂又是部分热载体,能有效提高气化效率,并维持炉内温度场的稳定。温度是蒸汽气化的关键,随着温度的升高,氢气的含量也增加。

(3) 以木屑为原料的下吸式气化炉气化,采用不同的气化剂气化效果明显不同,相比空气、富氧/蒸汽气化,高温蒸汽气化过程 H₂/CO 组分比由空气、富氧/蒸汽气化的 1.48、0.72 提高到 2.17,从而使气化效率和氢气含量大幅提高。

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